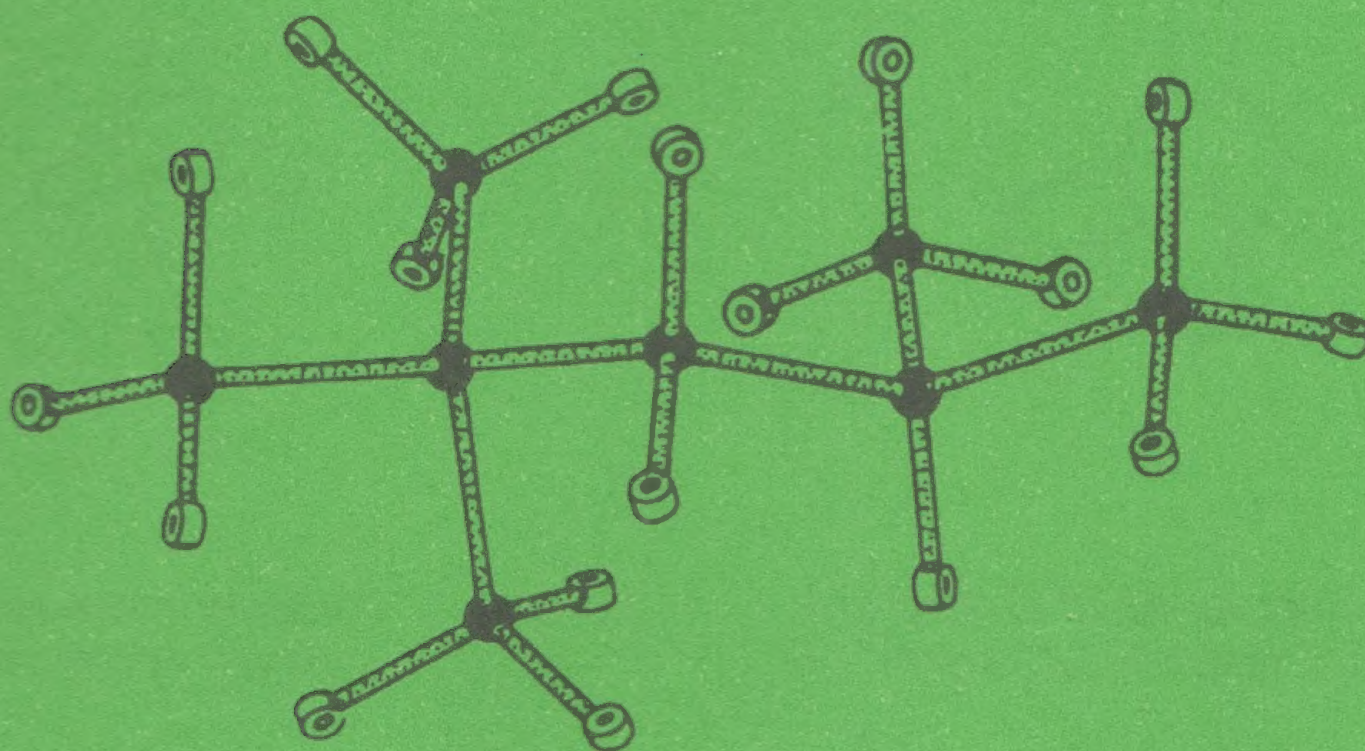




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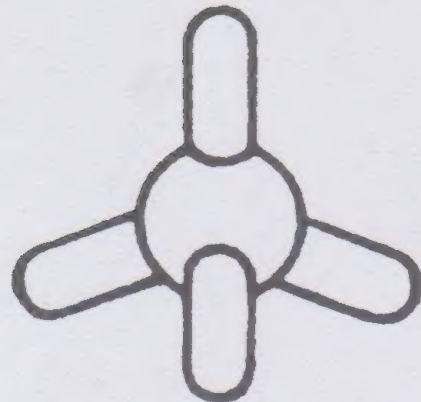


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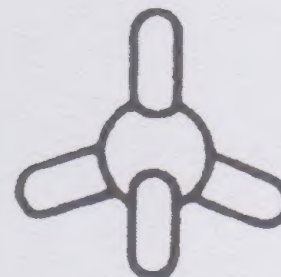
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Orbit atom
actual size



Minit atom
actual size



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Organic and inorganic chemistry

Instructions and notes on the use of the Minit and Orbit molecular building systems by **R S Lowrie** MA, D Phil, FRIC

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Introduction

The Minit and Orbit molecular building systems are designed to enable you to build molecular and crystal structures simply, accurately and at low cost. Molecules and crystals are represented by atom centres linked by tubes. This leads to a framework or skeletal representation of the molecule that is particularly good at showing the geometric structure of the substance. You can also perform 'reactions' with the models and examine different representations of valency and bonding.

The atoms consist of plastic centres having prongs set at the correct bond angles. Minit atom centres are 6mm in diameter and Orbit atom centres are 10 mm in diameter.





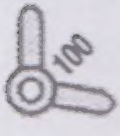

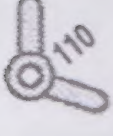
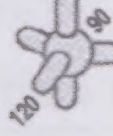
The centres are coloured according to the element or group of elements. In this booklet, an abbreviation is assigned to each colour that is usually the chemical symbol of the principal element that it represents. The principal elements and their colour coding are shown in Table I. Other colours are available including Blue-Green (Bromine), Dark Green (Iodine) and Dark grey (Iron).

Table I Colour coding of atom centres

| <i>Colour of atom centre</i> | <i>Principal element</i> | <i>Colour code</i> | <i>Colour of atom centre</i> | <i>Principal element</i> | <i>Colour code</i> |
|------------------------------|--------------------------|--------------------|------------------------------|--------------------------|--------------------|
| White | Hydrogen | H | Purple | Phosphorus | P |
| Black | Carbon | C | Green | Halogen | Hal |
| Blue | Nitrogen | N | Green | Chlorine | Cl |
| Red | Oxygen | O | Light green | Fluorine | F |
| Yellow | Sulphur | S | Silver | Metals | M |

A code letter is also used to describe each atom shape as shown in Table II. In the book text this letter is given following the colour code as a superscript. Thus a black (carbon) tetrahedral atom centre is coded C^k and a red (oxygen) univalent atom centre is coded O^a.

Table II Code letters denoting the shapes of atom centres in your set

| <i>Shape and description of atom centre</i> | <i>Code letter</i> | <i>Shape and description of atom centre</i> | <i>Code letter</i> |
|---|--------------------|---|--------------------|
|  univalent | a |  trigonal | j |
|  linear | b |  tetrahedral | k |
|  divalent, bent 100° | c |  octahedral | l |
|  divalent, bent 110° | d |  trigonal bipyramid | m |

Introduction to the bonds

Plastic tubes or straws representing bonds join the atom centres. Covalent bonds are normally represented by green or grey straws; white straws can be used for other purposes, such as hydrogen bonds. Multiple bonds may be simply represented by a single straw (not showing the multiplicity) or shown using multiple flexible tubes. With some sets, you can supplement the single straw with the pegs described on page 48 to show double bonds.

The length of the straw determines the bond length of the model. Table III gives straw lengths to the nearest 0.5 cm for common bonds and shows how these are calculated. The straw length is less than the model bond length to allow for the radii of the two atom centres (Orbit 0.5cm each, Minit 0.3 cm each). To study the concepts in this booklet modelling with three bond lengths is sufficient. You can use the straws provided in your set, choosing lengths nearest to those given in table III.

For more accurate modelling you can cut straws to your desired length. Straws pre-cut to other lengths may also be available from your supplier. For demonstration models you may choose to use a larger scale.

When substituting one atom or group for another on a model, it is wise to remove the associated bond, as the replacement group may require a bond of a different length.

Some sets include extra-rigid bonds in a slightly darker grey. These are for studying the conformations of cyclohexane and related structures.

Occasionally straws need to be pushed through the central hole of an atom centre. Only the thinner straws will fit.

Table III

Example Calculation of H-N bond length and straw lengths

| | | | | Minit | Orbit |
|-----------------------|---------|-------------------|---|--------|--------|
| Covalent radii | H 30 pm | Scale : 100 pm | = | 2.0 cm | 3.0 cm |
| | N 70 pm | Model bond length | | 2.0 cm | 3.0 cm |
| Internuclear distance | 100 pm | Atom centre size | | 0.6 cm | 1.0 cm |
| | | Straw length | | 1.4 cm | 2.0 cm |

Calculation of straw lengths to nearest half centimetre.

| <i>Bond</i> | <i>Sum of covalent radii</i> | | | <i>internuclear distance</i> | <i>Orbit length at 3cm per 100 pm</i> | <i>Minit length at 2cm per 100 pm</i> |
|------------------------------------|--------------------------------------|---|-----|----------------------------------|---|---|
| O-H | 67 | + | 30 | = 97 | 2.0 | 1.5 |
| N-H | 70 | + | 30 | = 100 | 2.0 | 1.5 |
| C-H | 77 | + | 30 | = 107 | 2.0 | 1.5 |
| C=O carbonyl | 67 | + | 55 | = 122 | 2.5 | 2.0 |
| C≡C | 62 | + | 62 | = 124 | 2.5 | 2.0 |
| S-H | 100 | + | 30 | = 130 | 3.0 | 2.0 |
| C≡N aromatic | 70 | + | 62 | = 132 | 3.0 | 2.0 |
| C=C | 67 | + | 67 | = 134 | 3.0 | 2.0 |
| C≡C aromatic | 70 | + | 70 | = 140 | 3.0 | 2.0 |
| C-O | 77 | + | 67 | = 144 | 3.5 | 2.5 |
| C-N | 77 | + | 67 | = 147 | 3.5 | 2.5 |
| C-C | 77 | + | 77 | = 154 | 3.5 | 2.5 |
| C-Cl | 77 | + | 99 | = 176 | 4.5 | 3.0 |
| C-S | 77 | + | 100 | = 177 | 4.5 | 3.0 |
| P-O | 110 | + | 67 | = 177 | 4.5 | 3.0 |
| Cl-Cl | 99 | + | 99 | = 198 | 5.0 | 3.5 |
| S-S | 100 | + | 100 | = 200 | 5.0 | 3.5 |
| Flexible straws for multiple bonds | | | | | 4.5 | 2.5 |

1 Principles of molecular shape

Molecules based upon the tetrahedron

The positions of the bonds from an atom are determined by the fact that the electron pairs forming the bonds repel one another electrostatically. For instance, tetrachloromethane, CCl_4 , has four electron-pair bonds $\text{C}-\text{Cl}$. If the bonds were arranged in a square planar fashion, there would be a 90° angle between adjacent bonds. Construct a model of the molecule CCl_4 , using a black carbon centre, C^k , and four green chlorine centres, Cl^a , linked by straws. Now thread a length of cotton through the chlorine centres so that all the chlorine atoms are joined to one another as in figure 1. Note that the shape formed is a triangular pyramid, or *tetrahedron*.

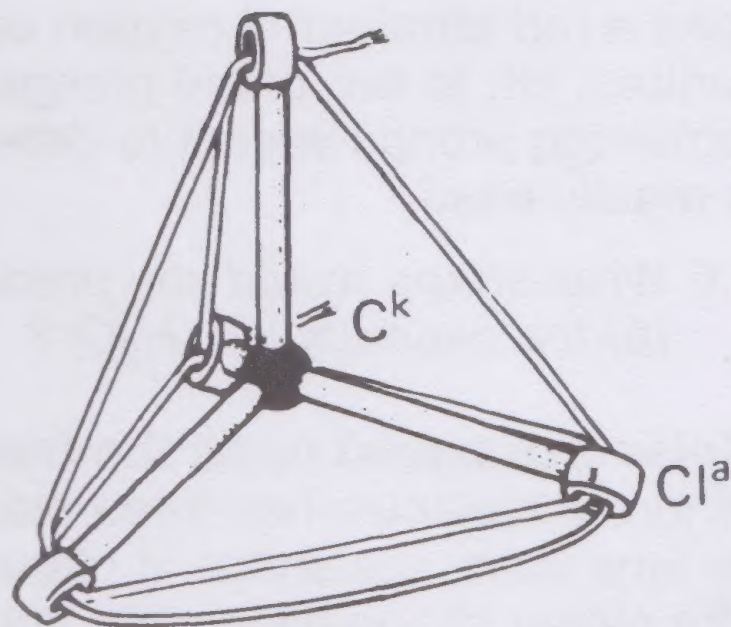


Figure 1
Tetrachloromethane, with cotton

- 1.1 *What is the angle between adjacent bonds? Measure the angles with a protractor, and check that they are all approximately equal.*
- 1.2 *Is it possible to devise a shape for CCl_4 in which all the bond angles are greater than this?*

The four chlorine atoms are at the corners of a tetrahedron with the carbon atom at its centre.

Ammonia, NH_3 , contains three electron-pair bonds, $\text{N}-\text{H}$, and one lone pair (figure 2).

The shape of the ammonia molecule is the result of the four electron pairs (three bond pairs and one lone pair) repelling each other. To construct a model, take a blue tetrahedral nitrogen centre, N^k , and attach hydrogen centres, H^a , to three prongs using straws. Leave the fourth prong unoccupied to depict the lone pair.

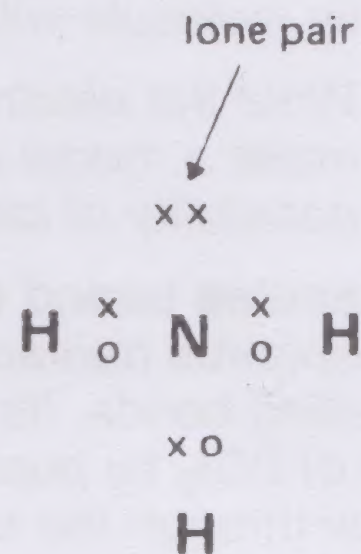


Figure 2 Ammonia

1.3 Describe the shape of the ammonia molecule.

1.4 What shape would you predict for the ammonium ion, NH_4^+ ?

Water, H_2O , has the electronic configuration shown in figure 3.

Take a red tetrahedral oxygen centre, O^k , and attach hydrogen centres, H^a , to two of the prongs using straws. Leave the two remaining prongs vacant to denote the lone pairs. The bent shape is readily seen.

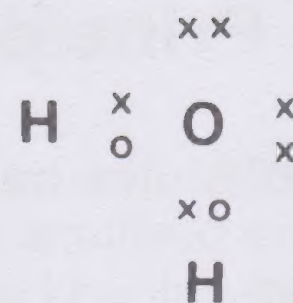


Figure 3 Water

1.5 What shape would you predict for (a) H_2S ;
(b) the oxonium ion, H_3O^+ ?

Molecules based upon the triangle

Where a molecule has three electron-pair bonds and no lone pairs, the shape is planar instead of pyramidal. The planar shape allows the angle between bonds to be 120° i.e. the separation is greater than in NH_3 . Boron trichloride, BCl_3 , is one example. The trigonal carbon centre, C^j , can be used to represent boron in this example. Simply join three chlorine centres, Cl^a , to it. Thread a length of cotton through the chlorine centres and note that an equilateral triangle results (figure 4). Compare the shape of this molecule with that of NH_3 .

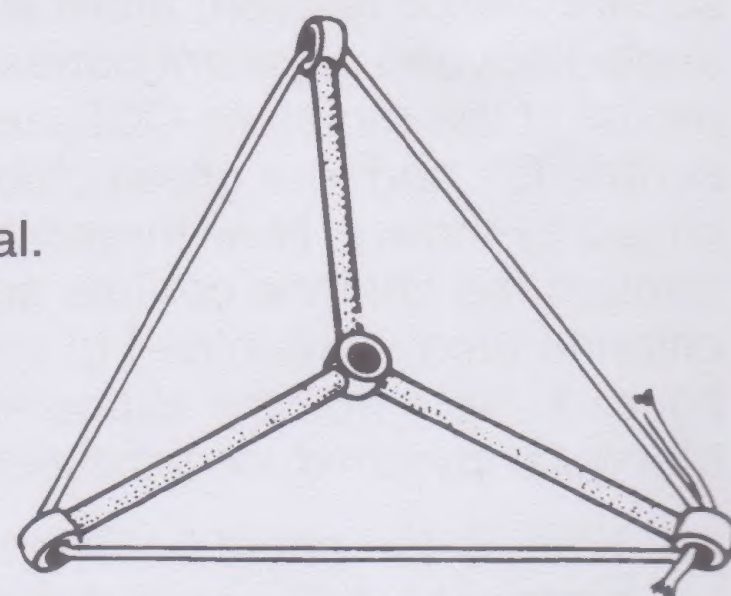


Figure 4 Boron trichloride, with cotton

1.6 Write the electronic configuration of PCl_3 , and make a model of it, taking into account the possibility of lone pair formation.

Molecules based upon the trigonal bipyramid

Phosphorus pentachloride, PCl_5 , has five repelling bonds. Its shape may be derived from that of BCl_3 by pushing a length of thin walled straw through the centre atom, as shown in figure 5, and adding a chlorine centre, Cl^a , to the end of each axial bond so formed.

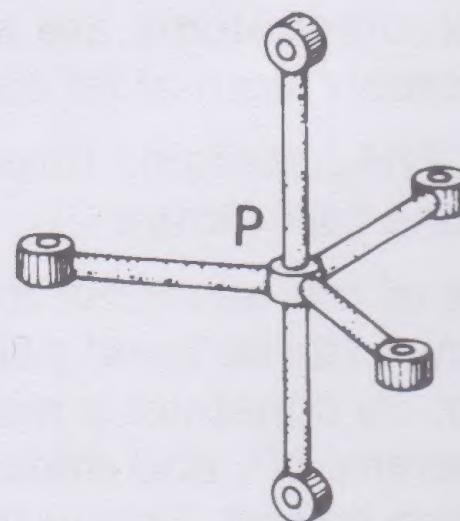


Figure 5 Phosphorus pentachloride

The kit provides a five-pronged phosphorus centre, P^m . Take one such centre and add five chlorine centres, Cl^a , to it. To enable the shape to be seen more clearly, take a length of cotton and thread it through the chlorine centres, as shown in figure 6. The shape is that of two pyramids base-to-base, i.e. a *trigonal bipyramid*.

- 1.7 Write electronic configurations for SF_4 and ClF_3 , and attempt to predict their shapes. Will the shapes be based upon the trigonal bipyramid?

Molecules based upon the octahedron

Sulphur hexafluoride, SF_6 , has six repelling bonds directed to the corners of an octahedron. Take the sulphur octahedral centre and attach six F^a centres to it (use Cl^a centres if F^a is not present). Thread a length of cotton through the fluorine centres as before and observe the octahedron produced.

- 1.8 Measure the angles between adjacent bonds.

- 1.9 Write the electronic structure, and hence predict the shape of BrF_5 .

Summary

The shapes of simple molecules are determined by the number of bonds plus the number of lone pairs in the valence shell of the centre atom.

Three bonds – a triangular molecule

Four bonds – a tetrahedral molecule

Three bonds plus one lone pair – a pyramidal molecule

Two bonds plus two lone pairs – a bent molecule

Five bonds – a trigonal bipyramid

Six bonds – an octahedral molecule

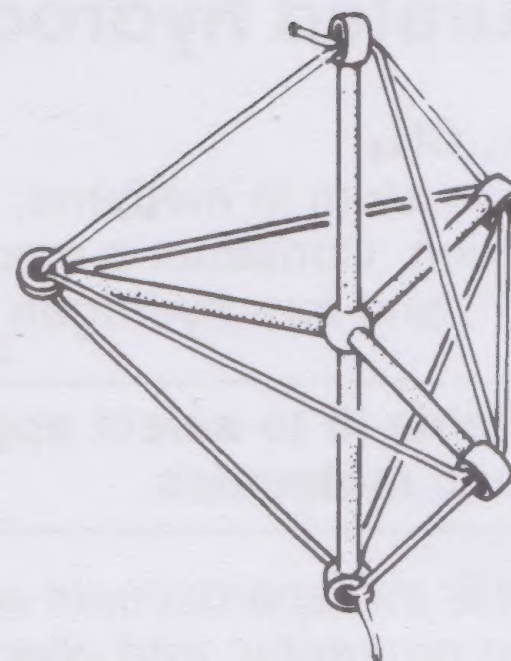


Figure 6 Phosphorus pentachloride, with cotton.

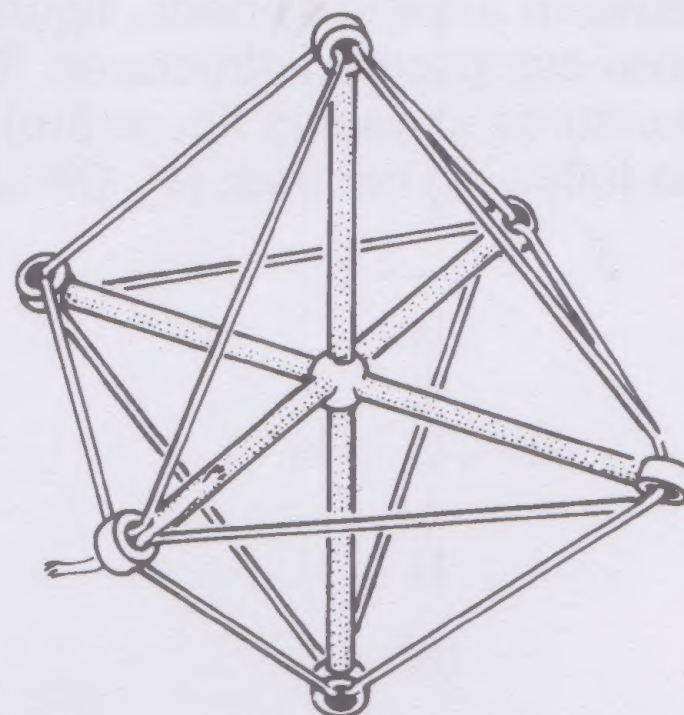


Figure 7 Sulphur hexafluoride, with cotton

2 Saturated hydrocarbons

Methane, CH₄

The carbon atom in methane, and in all 'saturated' structures is tetrahedral in configuration. Construct a model of the molecule CH₄ using a tetrahedral carbon centre, C^k, and four hydrogen centres, H^a.

Use table III to select appropriate bond lengths for this and other organic molecules.

2.1 *What is the approximate angle between adjacent bonds? Measure the angles with a protractor, and check that they are all the same.*

It is difficult to represent three-dimensional structures on paper, and it is conventional to show the bonds as if they lie in a plane, with an angle of 90° between adjacent bonds, figure 8(a). This method has limitations when depicting more complicated structures. To take a simple example, construct models of the structures shown in figure 8(b) and 8(c), dichloromethane, CH₂Cl₂. You will need the following centres: H^a, Cl^a and C^k.

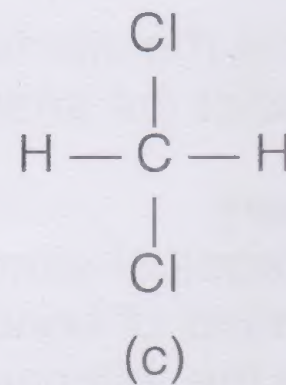
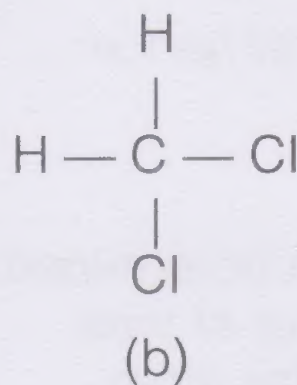
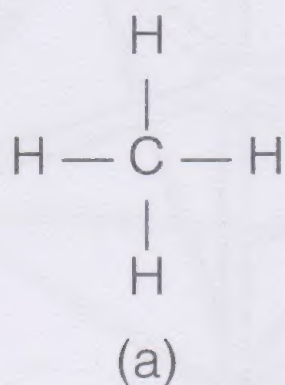


Figure 8 (a) Methane, (b) and (c) dichloromethane

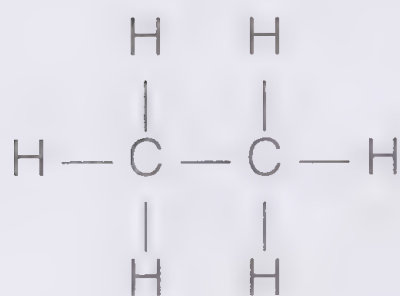
2.2 *Do structures (b) and (c) represent the same or different molecules? If you are in any doubt, rotate both models in such a way as to try to make them coincide.*

Ethane, C_2H_6 and propane, C_3H_8

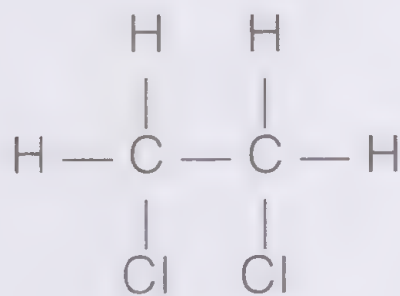
Construct a model of the molecule ethane, C_2H_6 , using two tetrahedral carbon centres, C^k , and six hydrogen centres, H^a , as in figure 9(a). Notice that the straws allow free rotation, so that the methyl groups CH_3 can be rotated relative to one another. Free rotation is typical of single-bond links.

Now construct a model of 1,2-dichloroethane, $C_2H_4Cl_2$, figure 9(b). Since the end groups can be rotated relative to one another, it is not possible to make more than one kind of molecule with the two chlorine atoms attached to different carbon atoms.

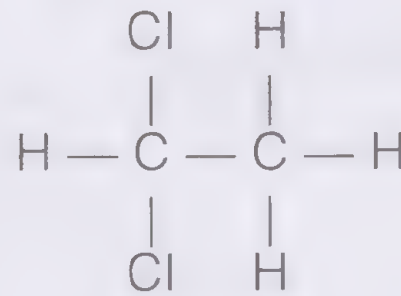
2.3 *Construct a model of 1,1-dichloroethane, figure 9(c). How many different kinds of molecule (isomers) are there corresponding to the molecular formula $C_2H_4Cl_2$?*



(a)



(b)

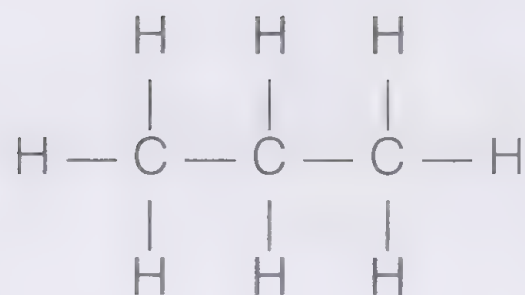


(c)

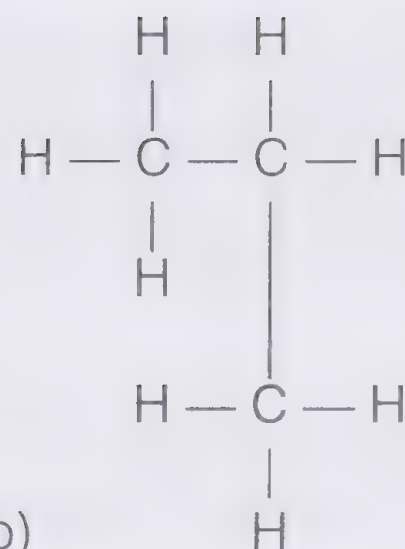
Figure 9 (a) Ethane (b) 1,2-dichloroethane (c) 1,1-dichloroethane

Now construct the two structures C_3H_8 depicted in figure 10. You have made molecules of the next alkane hydrocarbon, propane. Experiment with rotating the carbon-carbon bonds in the same way as you did with ethane structures.

2.4 *How many different structures can you make, corresponding to C_3H_8 , allowing for the fact that if one shape can be converted into another by free rotation, the substances represented are in fact the same?*



(a)



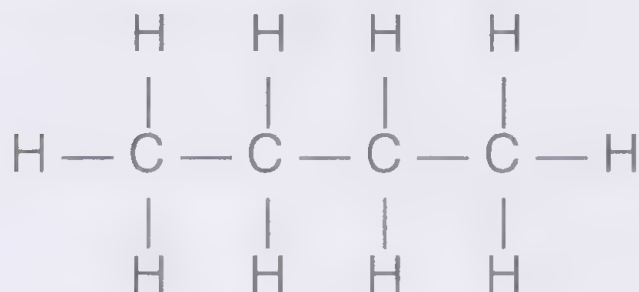
(b)

Figure 10 Two alternative representations of propane

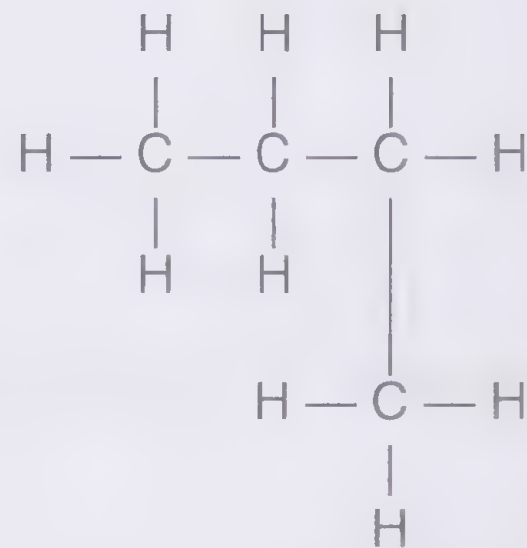
2.5 Try to work out on paper how many isomers of chloropropane $\text{C}_3\text{H}_7\text{Cl}$, can be made. Verify your predictions by constructing models.

2.6 How many isomers of dichloropropane, $\text{C}_3\text{H}_6\text{Cl}_2$, are there?

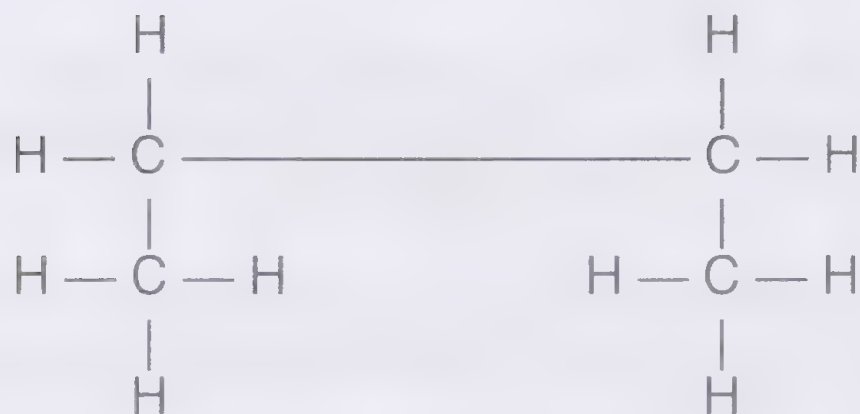
Butane, C_4H_{10}



(a)



(b)



(c)

Figure 11 Butane – three alternative representations

2.7 Examine the three different diagrams in figure 11. Do they in fact represent different molecules, allowing for free rotation of groups about the carbon-carbon bonds?

The three diagrams in figure 11 all contain a so-called 'straight-chain' of carbon atoms. This is usually depicted on paper as $C-C-C-C$ although if the atoms are not printed in a straight line it does not matter. There is only one straight chain isomer of butane, often called normal-butane or *n*-butane. The carbon 'backbone' is in fact not straight but zigzag, as your model should show. In a solid crystal, a regular zigzag is formed, but in the liquid and vapour phases, rotation can occur about all the bonds, and the backbone can twist into all sorts of shapes without the structure breaking up.

Construct another model of C_4H_{10} , this time using the 'branched-chain' configuration shown in figure 12. This represents an isomer of normal butane, sometimes referred to as iso-butane, although a better name is methylpropane.

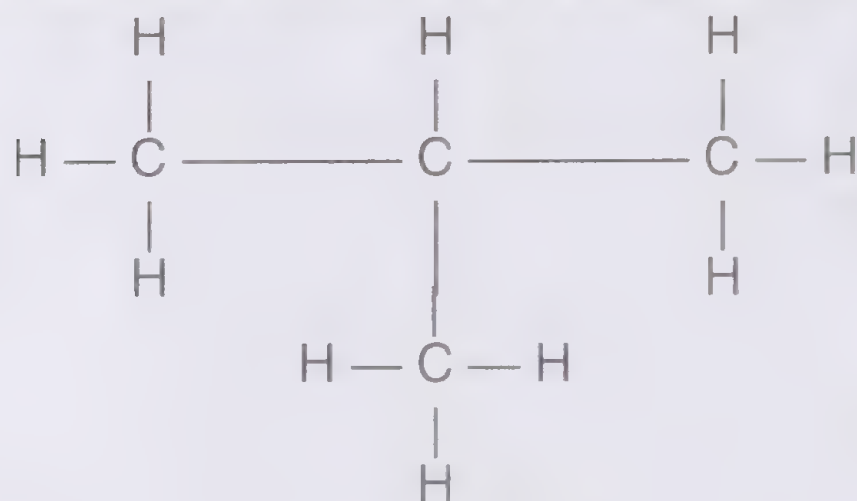


Figure 12 Methylpropane

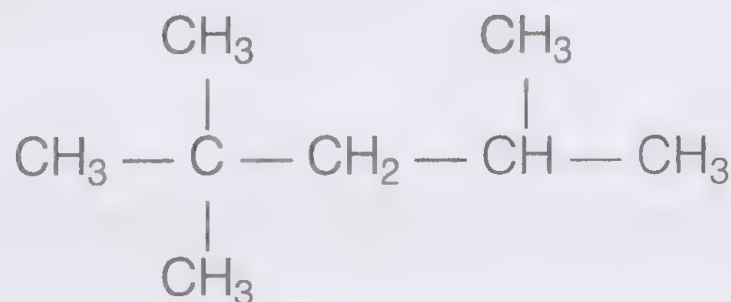


Figure 13 2,2,4-Trimethylpentane

2.8 Are there any other possible isomers of the molecular formula C_4H_{10} ?

Higher alkanes

Crude petroleum consists essentially of a mixture of alkanes with varying numbers of carbon atoms up to about 30. Most naturally occurring alkanes are 'straight-

chain', but 'branched-chain' alkanes are important commercially. For instance, 2,2,4-trimethylpentane is an important constituent of motor fuel.

Construct a model of 2,2,4-trimethylpentane.

2.9 *How many isomers do you think there are for 2,2,4-trimethylpentane?*

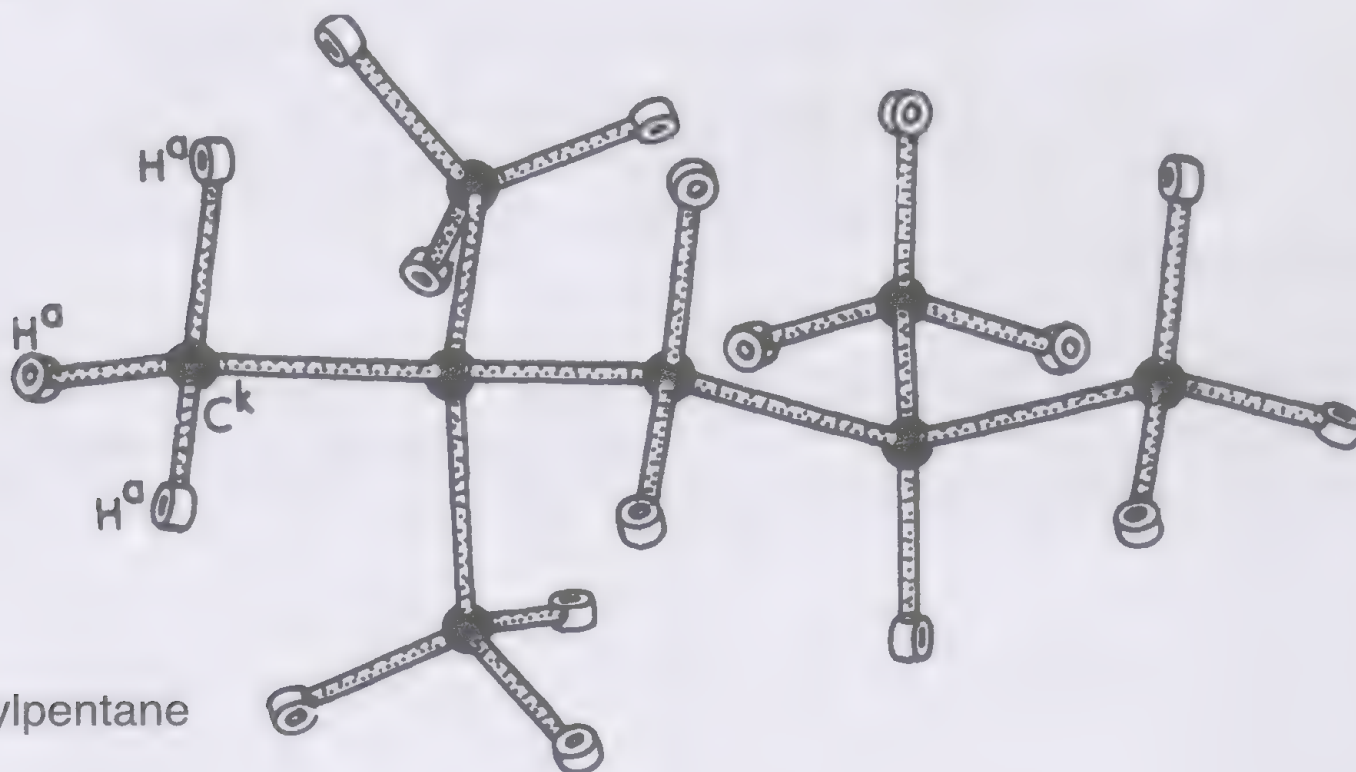


Figure 14 2,2,4-Trimethylpentane

3 Unsaturated hydrocarbons

Ethene, C_2H_4

Take two tetrahedral carbon centres, C^k , and join two hydrogen centres H^a to each. Now take two flexible straws and make a double bond linkage between the carbon centres, (figure 15). Each flexible straw represents an electron pair, in the same way as rigid straws do.

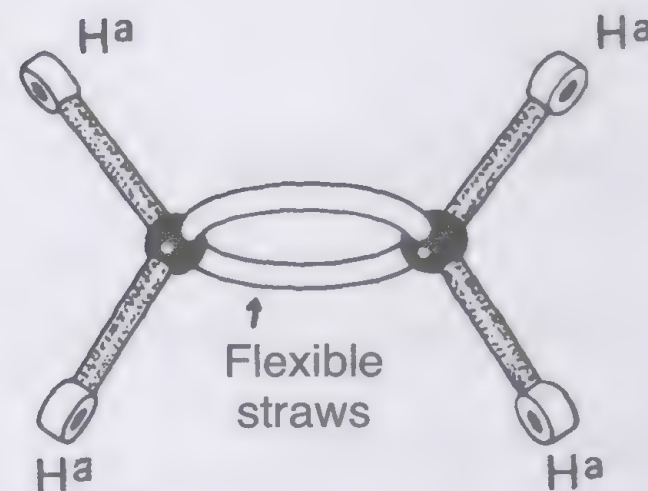


Figure 15 Ethene

3.1 *Do all the atoms lie in a plane?*

3.2 Can the molecule be rotated about the C–C bond?

3.3 How many electron pairs does each carbon atom have in ethene?

3.4 How many bonding electrons is this per carbon atom? Compare your answer to that for the carbon atoms in ethane (page 9).

Derivatives of ethene

Remove one hydrogen centre and straw from your model of ethene, and replace it by a chlorine centre, Cl^a, and straw. You now have chloroethene, C₂H₃Cl (known industrially as vinyl chloride).

3.5 If you had chosen a different hydrogen atom for substitution by chlorine, would this have resulted in a different structure?

3.6 How many isomers of C₂H₃Cl are possible?

Make up three models of chloroethene, C₂H₃Cl. Satisfy yourself that they are identical. (figure 16).

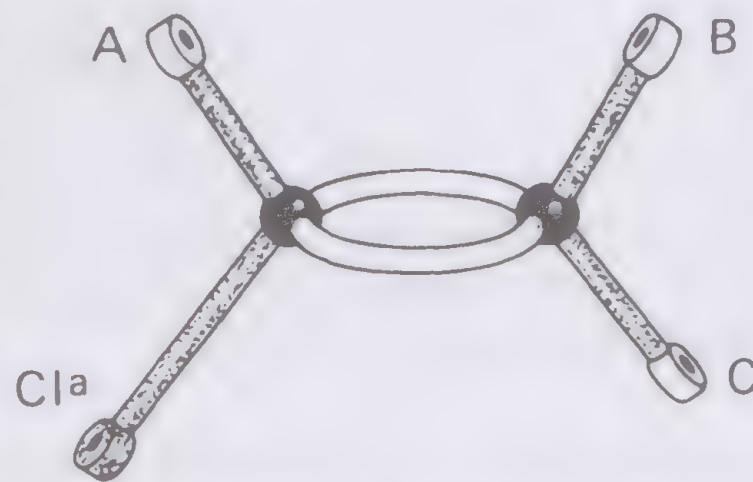


Figure 16 Chloroethene

Take the first model and substitute hydrogen centre A by a chlorine centre. Now take the second model, and substitute hydrogen centre B by chlorine. Finally take the third model and substitute hydrogen centre C by chlorine.

Call these three structures A, B and C respectively. They are all forms of dichloroethene, C₂H₂Cl₂, but they are not identical.

Model A has both chlorine atoms on carbon atom 1 and is called 1,1-dichloroethene. Models B and C both have their chlorine atoms on different carbon atoms: they are both named 1,2-dichloroethene. You will see however that B and C are different structures.

3.7 Can you convert B into C by twisting, without breaking the double bond?

Structures B and C represent what is known as geometric isomerism, which is a form of stereoisomerism. Geometric isomers have structures in which the atoms are similarly connected, but which differ as a result of restricted rotation of a bond in the molecule. If free rotation is made possible, one isomer may be converted into the other.

The isomer with both chlorine atoms on the same side is termed the *cis*-isomer (structure C) and the other structure is termed the *trans*-isomer (structure B). The complete name of structure C for instance is *cis*-1,2-dichloroethene.

Ethyne (acetylene)

Ethyne has a triple bond between its carbon atoms. Since there are no lone pairs on the carbon atoms, the configuration of the centres is linear. Construct a model of ethyne using three flexible straws between carbon centres, C^k , as shown in figure 17.

Note that considerable strain exists in the straws, representing the considerable reactivity of the C–C bond.



Figure 17 Ethyne

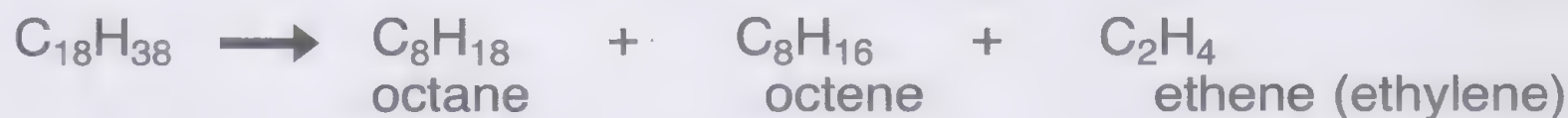
An alternative way of representing ethyne is to use linear C^b centres linked by a short rigid straw (figure 18).



Figure 18

Petroleum cracking

The term 'cracking' means breaking up a large molecule into smaller fragments. Crude oil contains too many large molecules (lubricating oil etc) and not enough smaller molecules (motor fuel). A typical equation for a cracking process is:



To make octene, use flexible straws to join the two end carbon centres in a double bond as in ethene (figure 19).

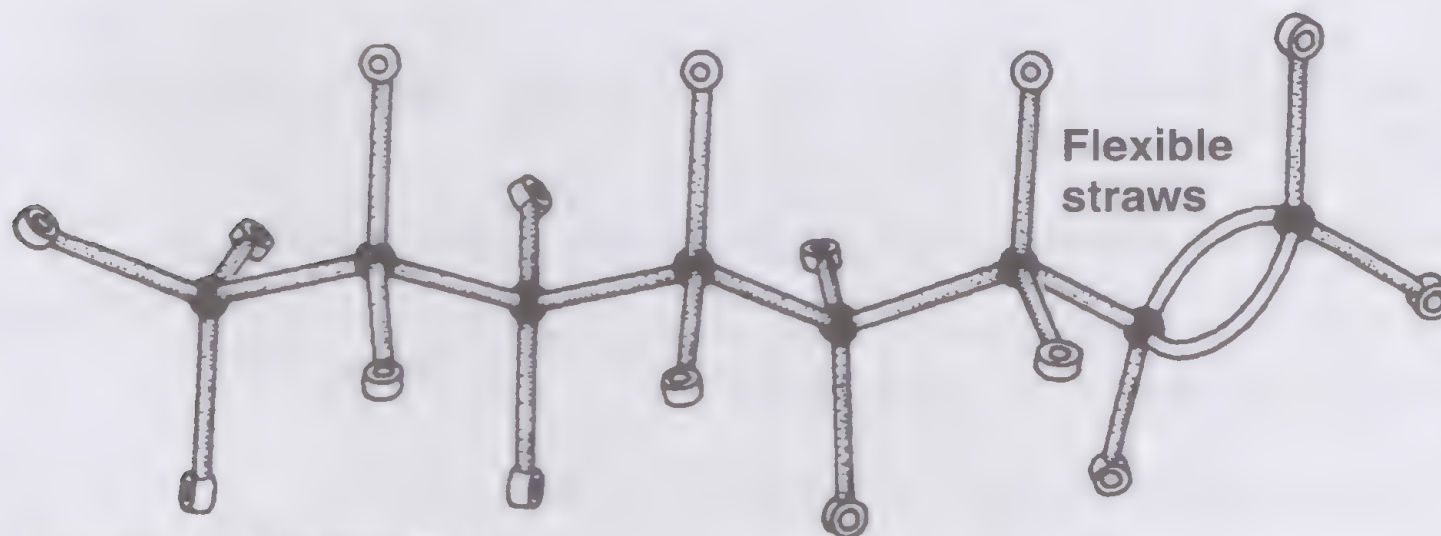


Figure 19 Octene C_8H_{16}

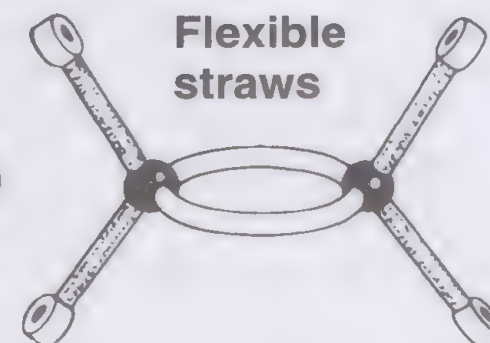


Figure 20 Ethene

4 Cyclic hydrocarbons

Simple cyclic structures

We have seen that so-called 'straight-chain' hydrocarbons are in fact zig-zag structures that can be distorted by free rotation. The tetrahedral bond angle (approximately 110°) also allows a variety of ring structures to be made. Saturated hydrocarbons with rings in their structures are referred to as cycloalkanes.

Cyclopentane, C_5H_{10}

Take five tetrahedral carbon centres, C^k , and join them in a 'ring'.

4.1 *Calculate the difference between the tetrahedral bond angle and the interior angle of the regular pentagon so formed.*

Notice at this stage that the carbon ring is completely planar. Now attach ten hydrogen centres, H^a , to the vacant prongs.

4.2 *Can the carbon-carbon bonds be freely rotated, as in a 'straight-chain' alkane? If not, why not?*

4.3 How many isomers of 1,2-dichlorocyclopentane is it possible to make, in which the chlorine atoms are attached to **adjacent** carbon atoms?

Cyclohexane, C_6H_{12}

Take six tetrahedral carbon centres, C^k , and join them in a 'ring'. Add twelve straws to the vacant prongs and attach twelve hydrogen centres, H^a .

In the Orbit system the extra rigid darker grey straws should be used for the C–C bonds

4.4 Is the resultant ring structure planar or puckered?

4.5 What is the angle between adjacent carbon-carbon bonds?

4.6 Can the carbon atoms be (a) freely, or (b) slightly, rotated relative to one another?

You will find that the six-membered ring is capable of two main shapes, or conformations. These are called the 'chair' form, figure 21 (a), and the 'boat' form, figure 21 (b), respectively. The hydrogen centres have been omitted from the figures for clarity.



Figure 21

Notice that a *slight* strain has to be applied to a given conformation in order to convert it, into the other conformation, even though bonds do not have to be broken. In practice, cyclohexane consists of a mixture of conformations in dynamic equilibrium and it is not possible to separate them as they interconvert too readily.

Larger rings

Experiment now with larger ring structures, for instance cycloheptane, C_7H_{14} and cyclo-octane, C_8H_{16} . The 'crown' conformation of cyclo-octane, figure 22, is also the conformation taken up by the S_8 ring in the crystalline forms of sulphur.

4.7 What is the bond angle between adjacent carbon atoms in cycloheptane and cyclo-octane?

4.8 It is not easy to synthesise very large rings of atoms, eg a C_{20} ring. Why should this be so?

Smaller rings

Using four tetrahedral carbon atoms and either normal or flexible straws, make cyclo-butane, the ring structure C_4H_8 .

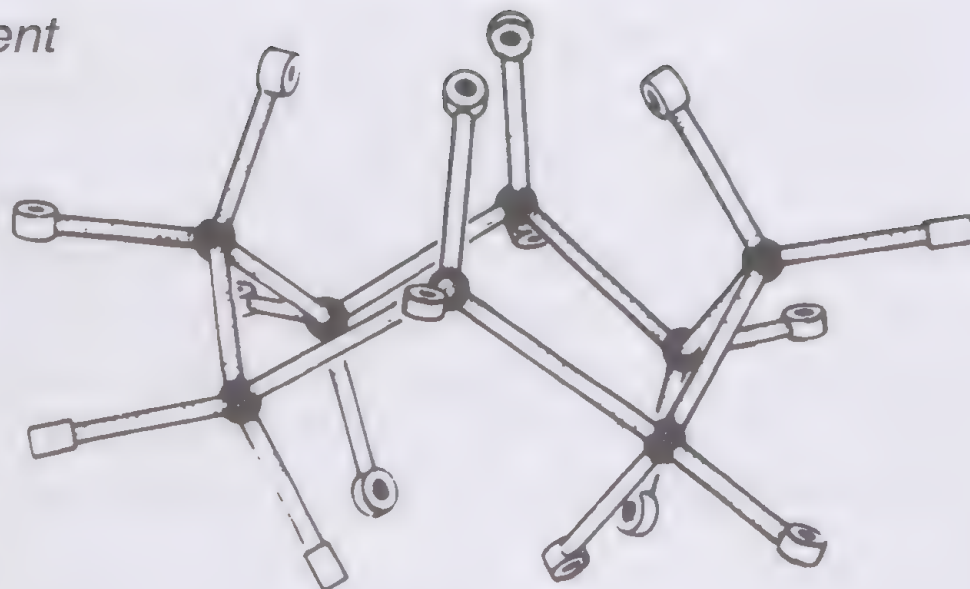


Figure 22 Cyclo-octane

4.9 Why do you suppose that cyclobutane is unstable and quite reactive?

The smallest ring, cyclopropane (C_3H_6), illustrates the same effect to an even more marked degree.

Summary

Saturated rings with five or more carbon atoms are unstrained. Saturated rings with six or more carbon atoms are non-planar, and can exist in more than one conformation. Saturated rings with four or less carbon atoms are strained due to distortion of bond angles from the tetrahedral positions. They are correspondingly reactive.

5 Functional groups in organic chemistry

This section summarizes the modelling of the principal functional groups in organic chemistry by considering their affect on butane.

Butane, $CH_3.CH_2.CH_2.CH_3$

Make a model of butane (Figure 11, page 10) with four tetrahedral carbon centres, C^k , and ten hydrogen centres, H^a .

1-Chlorobutane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$

If butane and chlorine are mixed and allowed to react in diffused light a number of products are obtained, among them 1-chlorobutane. To illustrate this substitution reaction make a molecule of chlorine, Cl_2 , by joining two Cl^a centres. Detach the chlorine centres from each other and their straw (these illustrate the presence of free chlorine atoms, which are thought to participate in the substitution reaction). Now detach a hydrogen centre with its straw from an end carbon atom of the butane molecule and attach it to one of the free chlorine atoms. Attach the other chlorine atom with its straw to the carbon chain.



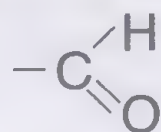
Butan-1-ol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

If 1-chlorobutane is warmed with aqueous alkali, OH^- (aq), a substitution reaction occurs. Make a model of the hydroxide ion, OH^- , using a two-pronged oxygen centre, O^d , an H^a centre and two straws. The straw with no atom attached represents the electron pair on the oxygen atom giving its negative charge. Detach the chlorine centre and straw from 1-chlorobutane and attach the OH^- group.



Butanal, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$

If butan-1-ol is oxidized by distilling with dilute aqueous sodium dichromate, the end-group $-\text{CH}_2\text{OH}$ is oxidized to the group



From your model of butan-1-ol remove the OH group and a hydrogen from the end carbon and make a carbonyl group, $\text{C}=\text{O}$, in its place, using an oxygen centre, O^d , and two flexible straws. (figure 23a).

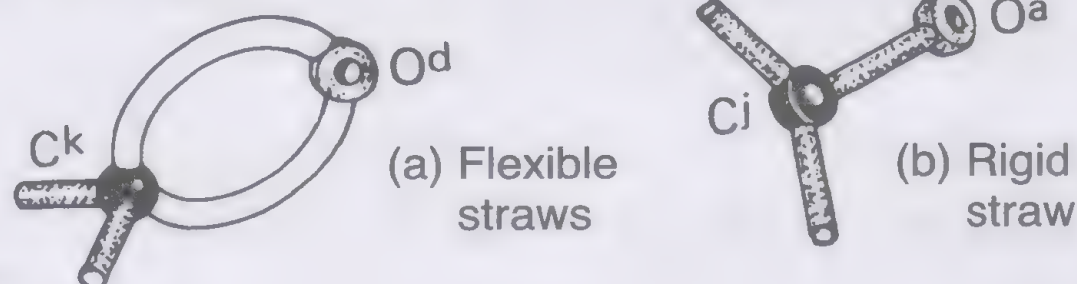
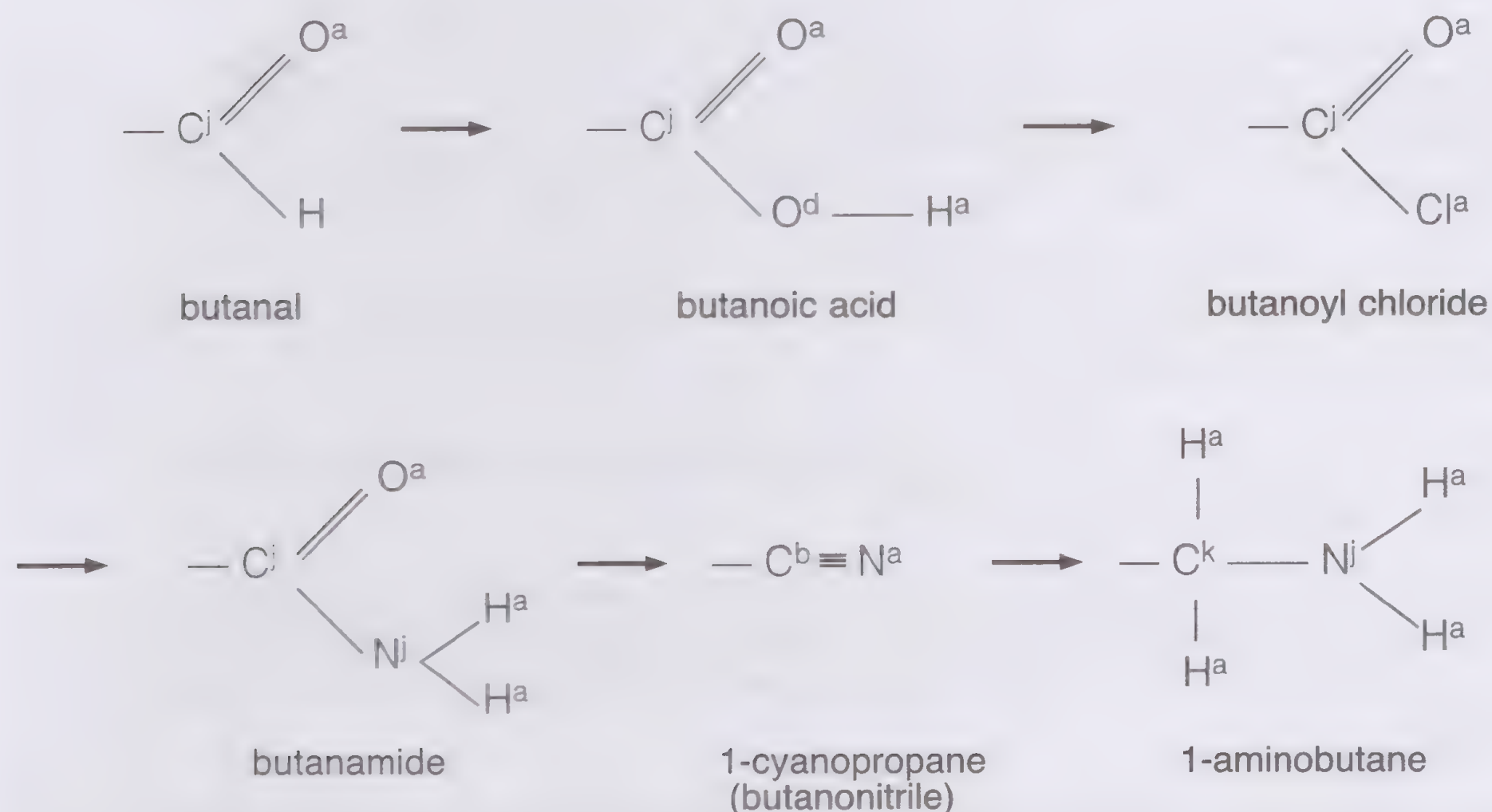


Figure 23 Carbonyl group

An alternative way of representing the carbonyl group is by using C^j and O^a centres linked by a rigid straw (figure 23b). In this booklet double bonds are only shown with flexible straws where restricted rotation is important.

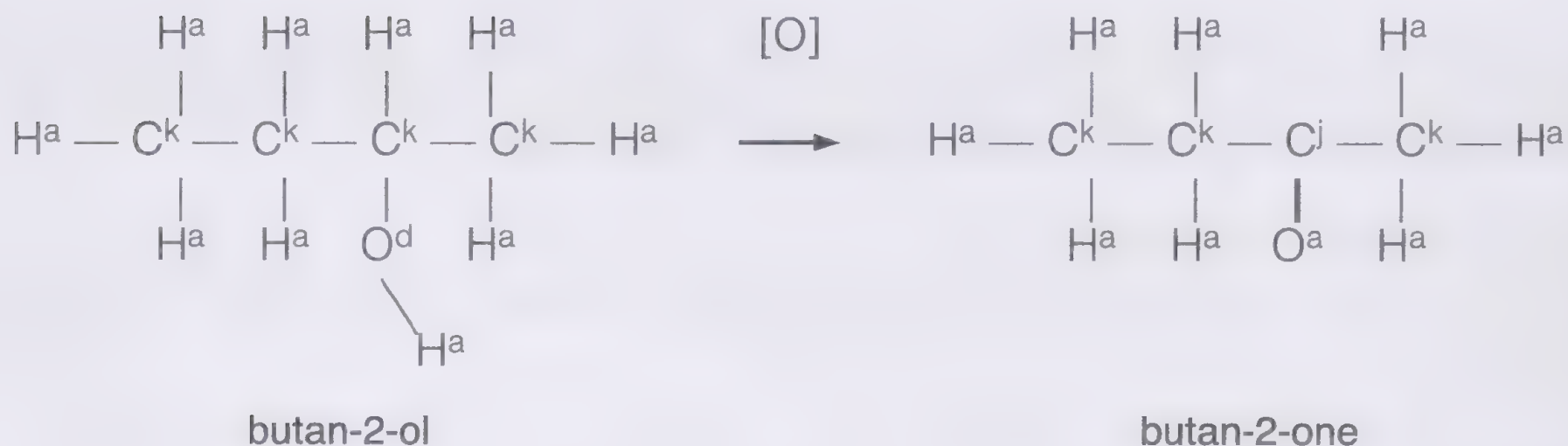
Further functional groups

Using the same carbon chain, the following further stages in the synthetic route can be effected:



Secondary alcohols and ketones

If 2-chlorobutane is used in place of 1-chlorobutane as the starting material, aqueous alkali gives butan-2-ol, and oxidation of this gives butanone. Further oxidation cannot occur however without the carbon chain being broken.



Isomers of butanol

Construct a model of butane, figure 24. In this molecule there are essentially two different types of hydrogen atom:

- Those attached to the end atoms, ie part of a methyl group, $-\text{CH}_3$ (labelled '1' on the diagram).
- Those attached to the other carbon atoms, ie part of a methylene group, $-\text{CH}_2-$, (labelled '2' on the diagram).

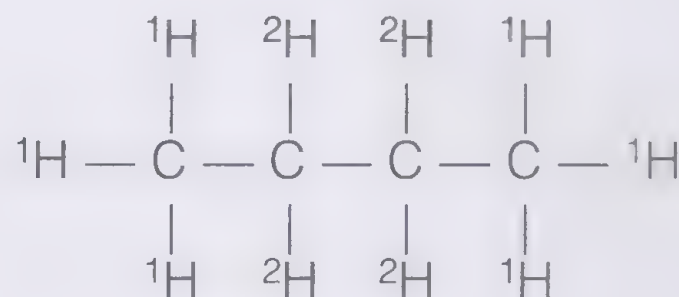


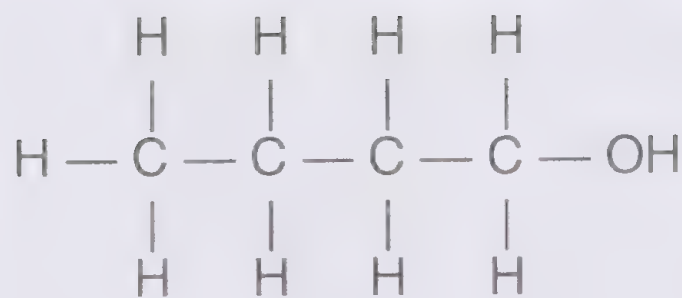
Figure 24 Butane

An alcohol may be regarded as derived from the parent hydrocarbon by the replacement of a hydrogen atom by a hydroxyl group, $-\text{OH}$. Construct a model of a hydroxyl group, use a two-bonded oxygen centre, O^d , with a hydrogen atom attached.

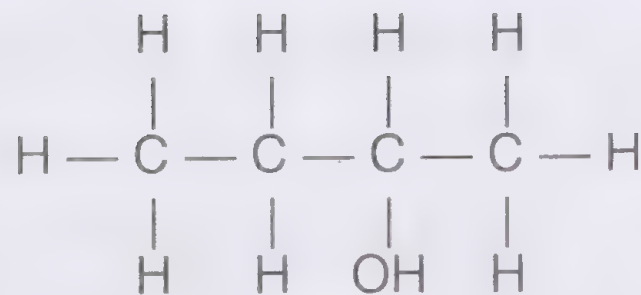
5.1 *Why are the two bonds leading from the oxygen atom set at an angle instead of in a straight line?*

Two molecules of butanol exist, based upon the straight-chain hydrocarbon butane.

- (1) Any one of the hydrogen atoms labelled '1' in figure 24 may be replaced by a hydroxyl group, making butan-1-ol, figure 25(a).



(a)



(b)

Figure 25 (a) Butan-1-ol, (b) Butan-2-ol

(2) Any one of the hydrogen atoms labelled '2' in figure 24 may be substituted by a hydroxyl group, making butan-2-ol, figure 25(b).

Construct models of the molecules in figures 25(a) and 25(b),

Taking the branched chain isomer of butane and substituting different hydrogen atoms with a hydroxyl group can make further isomers of molecular formula $\text{C}_4\text{H}_{10}\text{O}$.

5.2 How many different 'kinds' of hydrogen atom are there in figure 26? (Examine each hydrogen atom in turn and see what it is attached to and what type of group it belongs to).

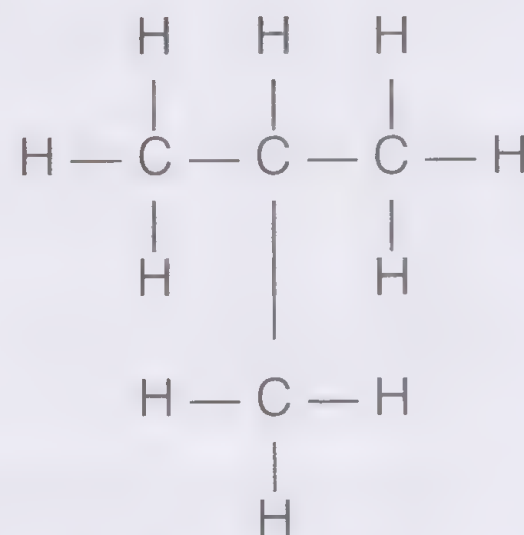


Figure 26 Methylpropane

Now construct models of the alcohols $\text{C}_4\text{H}_{10}\text{O}$ based upon the branched chain in figure 26.

Ethers of molecular formula $\text{C}_4\text{H}_{10}\text{O}$

If you have reasoned correctly so far, you should have managed to construct four different models of alcohols (substances containing the hydroxyl group, $-\text{OH}$) of molecular formula $\text{C}_4\text{H}_{10}\text{O}$; two based upon the straight chain of carbon atoms and two upon the branched chain.

This however does not represent all the possible ways of connecting together the atoms $\text{C}_4\text{H}_{10}\text{O}$. A further series of models can be constructed, containing the link $\text{C}-\text{O}-\text{C}$.

Such compounds consist of two alkyl groups linked to an oxygen atom and are known as ethers.

Figure 27 shows a simple ether ethoxyethane, which is isomeric with the butyl alcohols. Construct a model of this, using a bent oxygen centre, O^d .

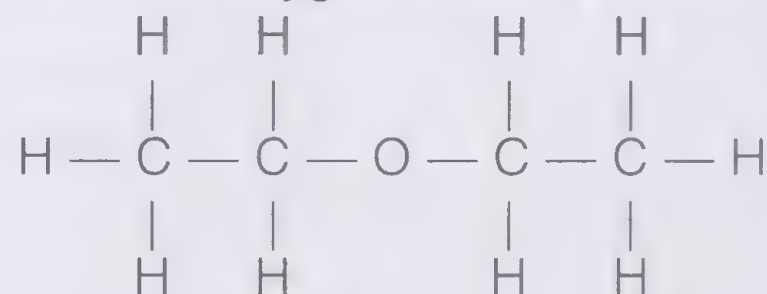


Figure 27 Ethoxyethane

5.3 *How many other ethers can be made, of the same molecular formula, ie isomeric with ethoxyethane? Try to predict the possibilities on paper, and then construct models. Check carefully to see that you have not made two the same.*

Definitions

- (1) The relationship between compounds of the same molecular formula but containing different functional groups is sometimes known as functional group isomerism.
- (2) The relationship between isomers which differ only in the nature of their alkyl groups attached to a given group is sometimes known as metamerism.

Further suggestions

Use the model kit to help answer the following questions:

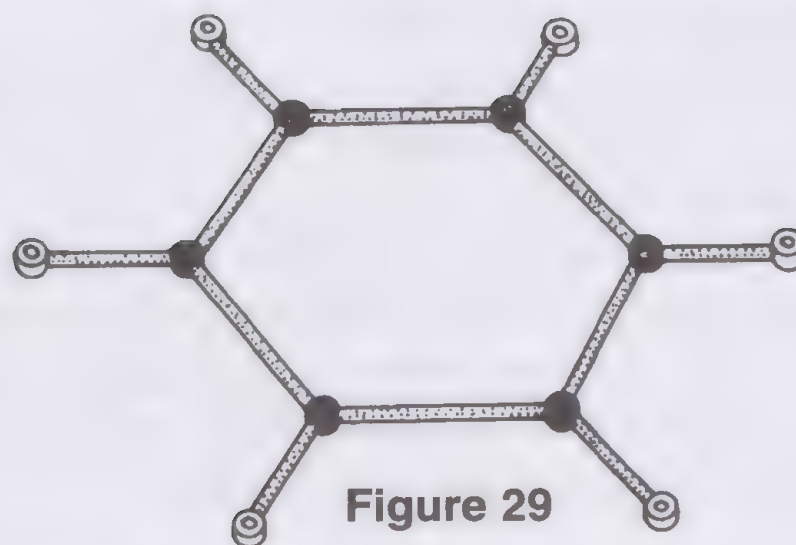
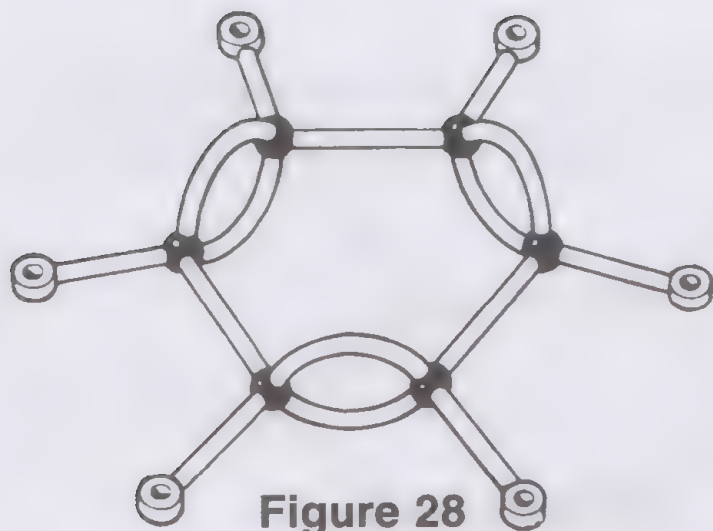
5.4 *How many isomers of molecular formula C_3H_8O are possible? How many of these are alcohols, and how many ethers?*

5.5 *How many isomers of molecular formula $C_5H_{12}O$ are possible? Try to work this out on paper, and check your predictions by constructing models.*

6 Benzene and its derivatives

Benzene, C_6H_6

The true shape of the benzene molecule is a regular hexagon, with 120° bond angles throughout. An approximation to its structure may be obtained by constructing a ring using six tetrahedral centres, C^k , linked alternately by double and single bonds. Six hydrogen centres H^a are then joined to the remaining prongs (figure 28).



A better representation is to use six trigonal carbon centres, C_i , in the form of a planar ring, with six hydrogen centres attached to the remaining prongs (figure 29). You can also represent the presence of the p-orbitals that form the pi bonding in benzene by pushing thin-walled straws through the holes in the carbon centres such that half the straw appears on each side.

Chlorobenzene, C_6H_5Cl

Detach one hydrogen centre, together with its bond, from your benzene model, and attach a chlorine centre, Cl^a . This is a model of chlorobenzene.

6.1 *Is isomerism of chlorobenzene possible?*

Dichlorobenzene, $C_6H_4Cl_2$

Detach another hydrogen centre (anyone will do) from your chlorobenzene model, and replace with chlorine as before. You now have a model of one of the isomers of dichlorobenzene.

6.2 *How many possible isomers exist for dichlorobenzene?*

Make models of as many isomers as you can and check carefully (by rearranging them and turning them over) that they are all different. Figure 30 shows one possibility, and its name. What are the others?

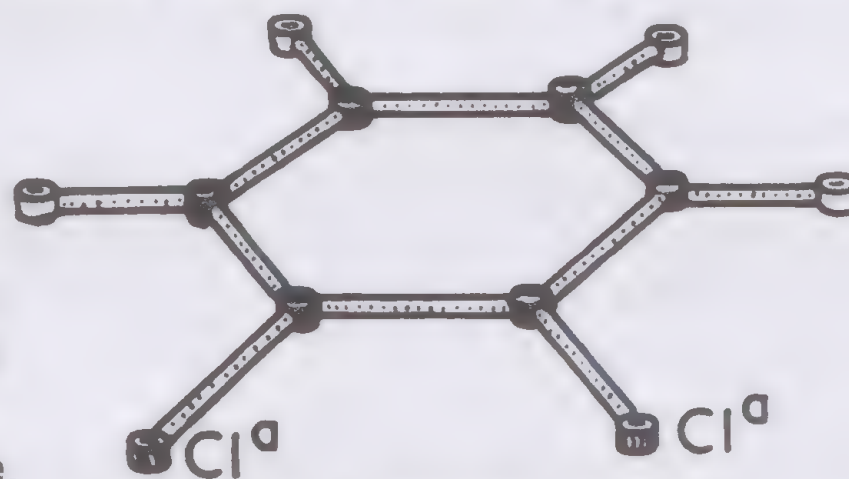


Figure 30 1,2-Dichlorobenzene

Nitrobenzene, $C_6H_5NO_2$

The action of nitronium ion, NO_2^+ , present in a mixture of concentrated nitric and sulphuric acids, converts benzene to nitrobenzene. The nitro group, $-NO_2$ has no lone pairs on the nitrogen atom and therefore has a trigonal centre Nj. Make a nitro group by joining two oxygen centres, O^a , to the nitrogen centre, and attach this group to the benzene ring, having first removed a hydrogen centre.

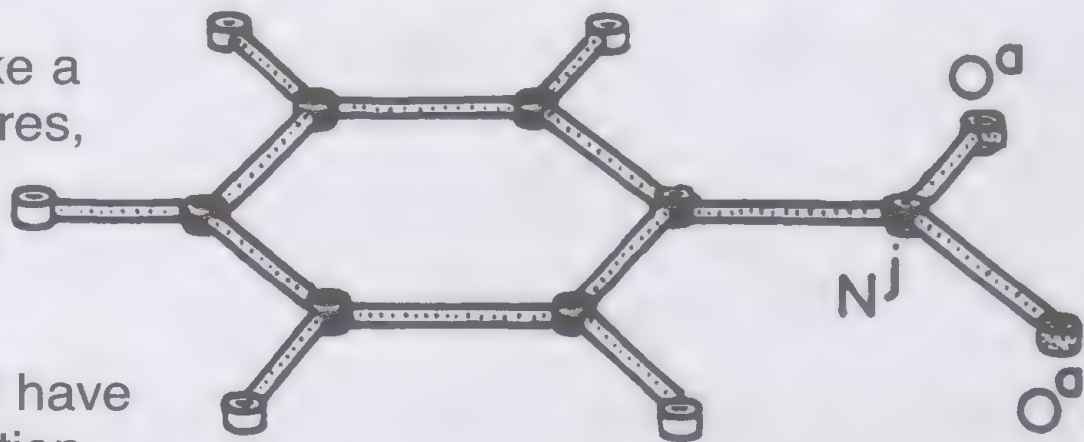


Figure 31 Nitrobenzene

The carbon-nitrogen bond does in fact have some π -bond character, due to interaction of the π -electrons in the carbon ring with the nitro group.

6.3 How many isomers of dinitrobenzene, $C_6H_4(NO_2)_2$, are possible? Name them.

Phenylamine (aniline) $C_6H_5NH_2$

Reduction of nitrobenzene in strongly acid conditions gives the phenyl ammonium ion, $C_6H_5NH_3^+$.

6.4 What will be the probable configuration of the bonds around the nitrogen atom in $C_6H_5NH_3^+$? Will a π -bond between the carbon and nitrogen atoms be possible?

Make a model of the phenylammonium ion, using the correct nitrogen centre.

Methylbenzene, $C_6H_5CH_3$

Hydrocarbon derivatives of benzene are present in coal tar. The simplest is methylbenzene. To make a model, start with benzene and replace a hydrogen centre with a methyl group $-CH_3$. Use a tetrahedral carbon centre, C^k , for the methyl group.

6.6 How many isomers containing a benzene ring exist corresponding to the molecular formula C_8H_{10} ? Make models, and name them.

Phenol, C_6H_5OH

The oxygen atom in phenol possesses two lone pairs and its configuration is therefore bent (page 8). Construct a hydroxyl group $-OH$ using an oxygen centre, O^d , and a hydrogen centre, H^a . Take a model of benzene, remove a hydrogen atom and its bond and attach a hydroxyl group.

Benzenesulphonic acid, $C_6H_5SO_2OH$

Benzenesulphonic acid may be regarded as derived from sulphuric acid (page 41) by the replacement of a hydroxyl group in the latter by a phenyl group, $-C_6H_5$. Construct a model of sulphuric acid, H_2SO_4 , and then remove a hydroxyl group from it. Remove a hydrogen centre from a model of benzene and join the two resultant groups.

Benzenecarboxylic acid (Benzoic acid), C_6H_5COOH

Benzenecarboxylic acid contains the carboxyl group, which comprises a carbonyl group joined to a hydroxyl group. Construct a carbonyl group, using a trigonal carbon centre, C^j , joined to an oxygen centre, O^a . Join this group to a hydroxyl group. Removing a hydrogen atom and straw from a model of a benzene molecule, and connecting instead the carboxyl group makes the structure of benzenecarboxylic acid.

7 Polymerization

Introduction

Polymers are macromolecules built by the linking together of monomer units. The following are some of the ways in which monomers (represented by M and N) can be linked together.

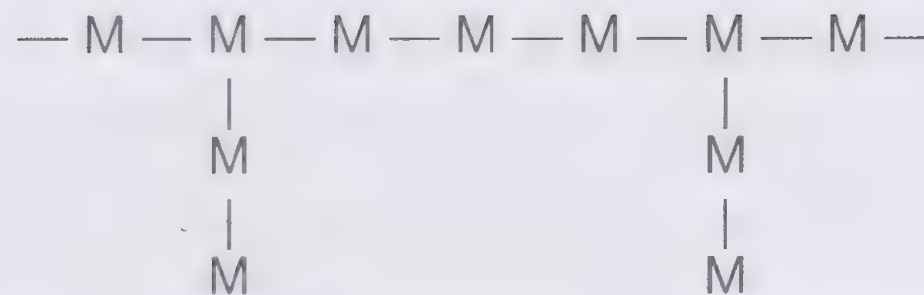
(i) Simple linear polymer



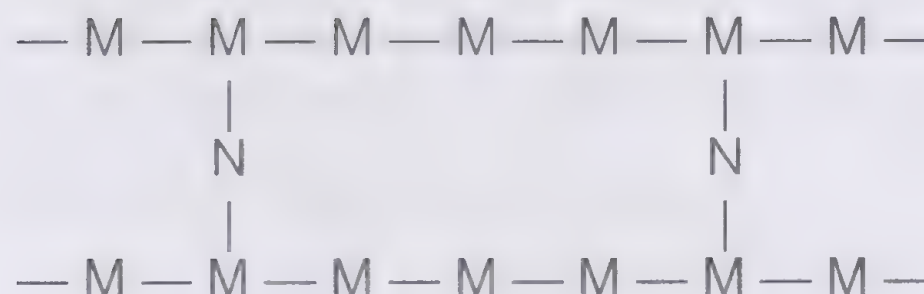
(ii) Simple linear co-polymer



(iii) Simple cross-linked polymer



(iv) Cross-linked co-polymer



Simple linear polymers

Polyethene (polythene) is formed by the addition polymerization of ethene (page 12). Similarly, tetrafluoroethene, C_2F_4 , polymerizes to give polytetrafluoroethene, PTFE, $(C_2F_4)_x$.

To make models of these two simple polymers, start by constructing a chain of carbon atoms, using tetrahedral carbon centres, C^k . For polythene, connect hydrogen centres, H^a , to the unoccupied carbon prongs. For PTFE, connect green centres (Cl^a will serve here).

Polypropene is the addition polymer made by the polymerization of propene, $\text{CH}_3-\text{CH}=\text{CH}_2$. The monomer is made by constructing ethene, C_2H_4 , as described on page 12, and then substituting one hydrogen centre with a methyl group, $-\text{CH}_3$. The methyl group uses a tetrahedral centre, C^k , linked to three hydrogen centres.

Compounds of the general formula $\text{CH}_2 = \text{CH}_2\text{X}$ can be polymerized to give two different forms each having a regular structure. Figure 32 shows (a) the *isotactic* form, in which all the X groups (in these figures X is a methyl group) lie on the same side of the polymer chain; (b) the *syndiotactic* form, in which the X groups lie on alternate sides. There is a third form, the *atactic* form, in which the X groups are arranged at random.

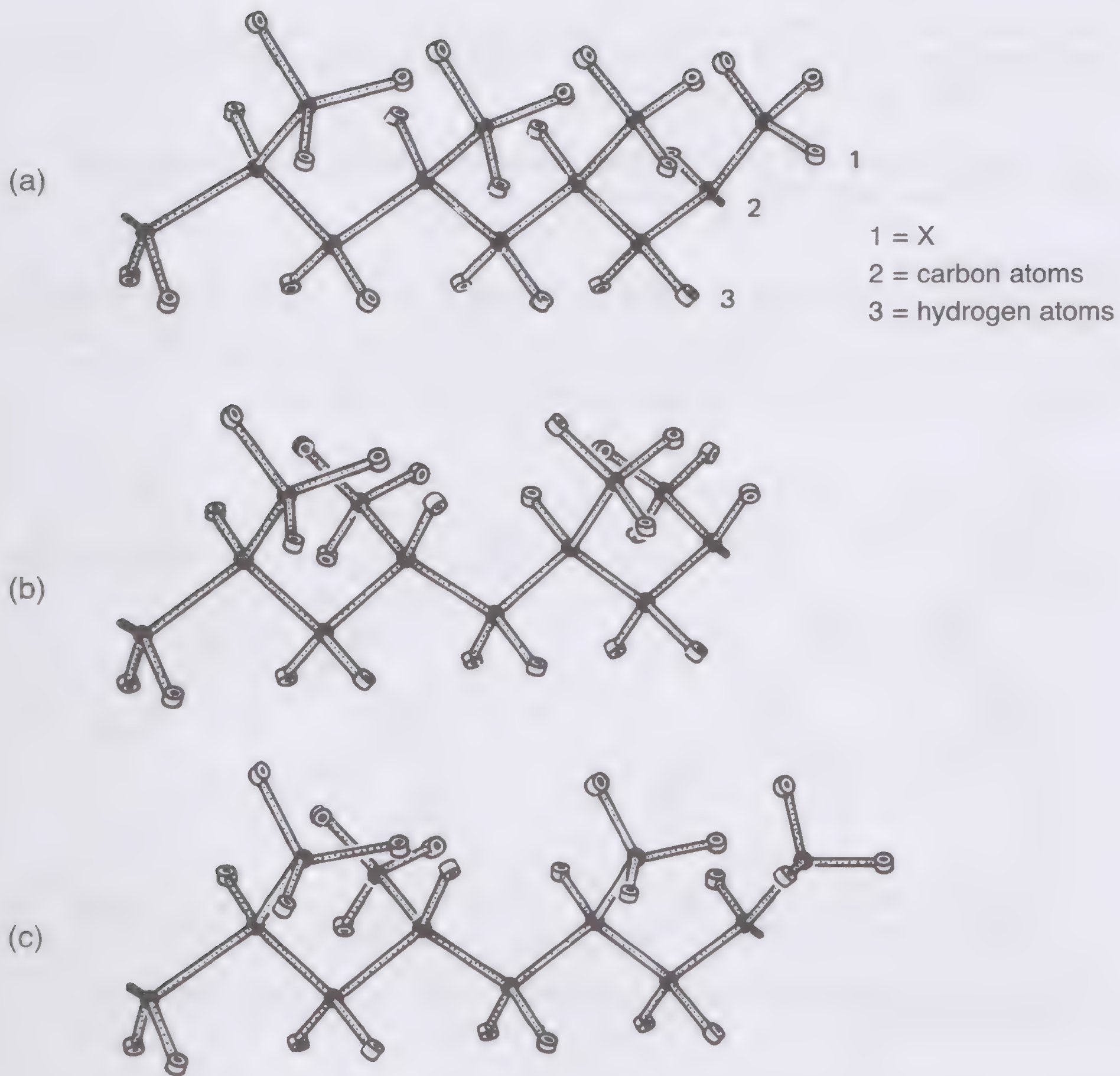


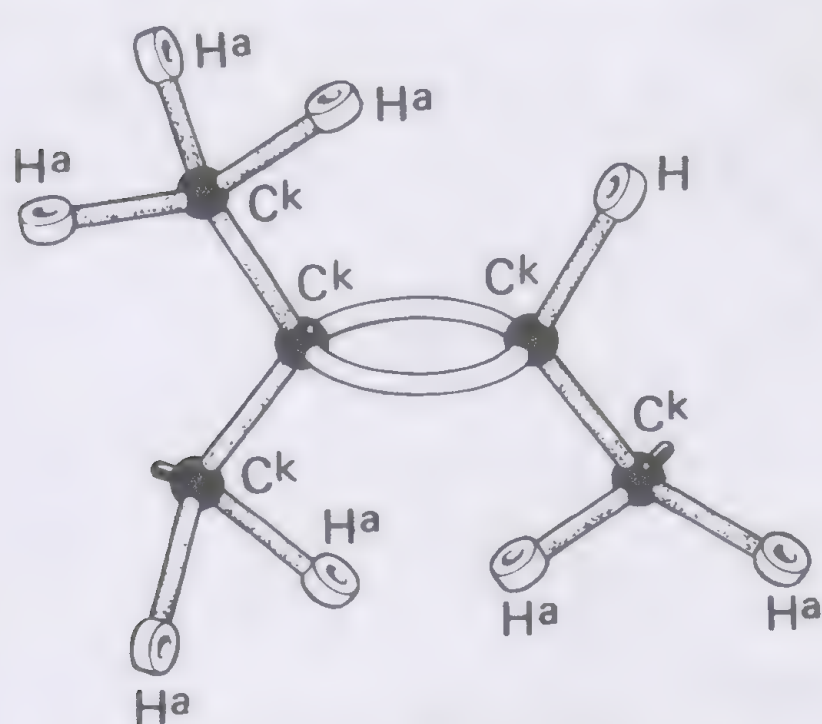
Figure 32 Polymers (a) *isotactic*, (b) *syndiotactic*, (c) *atactic*

Polypropene is made in forms (a) and (c), where X = methyl. To make models of the forms start with a model of polythene, and replace hydrogen atoms with methyl groups as in figure 32.

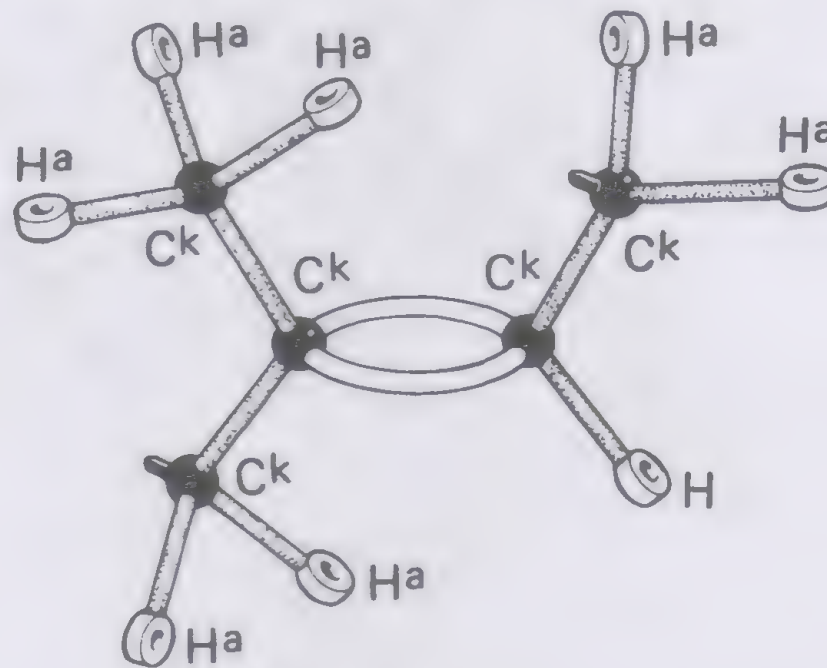
Note that these polymers all have saturated structures and hence are all highly unreactive compared with their monomers.

Synthetic rubbers

Natural rubber is an *elastomer*, containing molecules made up on average of about 10^4 units of isoprene $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$. Isoprene can also be polymerized synthetically in isotactic form. The double bonds rearrange themselves and the linking bonds may be either *cis* or *trans* to one another (page 14).



(a) *cis*-isoprene, which corresponds closely to natural rubber



(b) *trans*-isoprene, which corresponds closely to gutta percha

Figure 33

Make models of the monomer units (a) and (b), using C^k centres and flexible straws where indicated.

To make a model of natural rubber, connect several units (a) together. The elastic property of rubber is due to weak attractive forces between adjacent chains, coupled with a small degree of cross-linking.

Nylon – a co-polymer

The term 'Nylon' embraces several different condensation co-polymers of a similar type. One form, Nylon 6 – 6, is made by the condensation reaction between molecules of 1,6-diaminohexane $\text{H}_2\text{N} \cdot (\text{CH}_2)_6 \cdot \text{NH}_2$, with hexane-1,6 diol chloride (adipyl chloride), $\text{Cl} \cdot \text{CO} \cdot (\text{CH}_2)_4 \cdot \text{CO} \cdot \text{Cl}$, with the elimination of hydrogen chloride. The repeating unit is $-\text{NH} \cdot (\text{CH}_2)_6 \cdot \text{NH} \cdot \text{CO} \cdot (\text{CH}_2)_4 \cdot \text{CO}-$. Figure 34 shows a model of the unit.

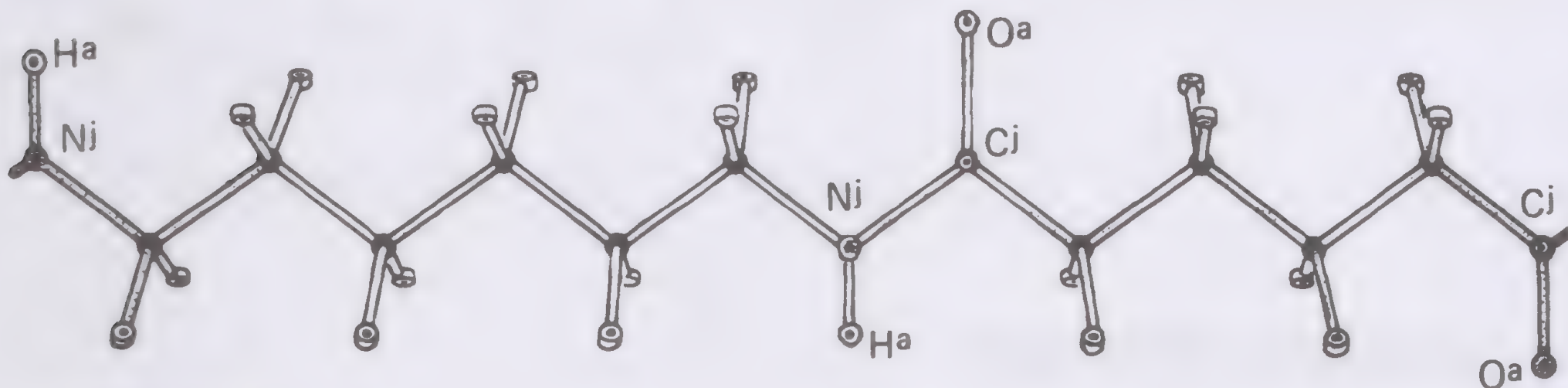


Figure 34 Nylon

Perspex

Figure 35 shows you how to make a model of the 'Perspex' monomer, methyl methacrylate. The active double bond is shown using flexible straws, just as with ethene.

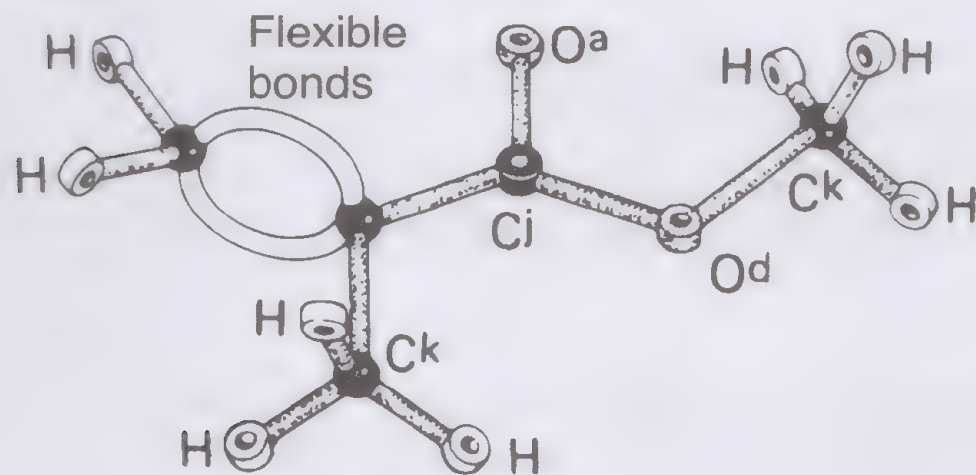


Figure 35 Perspex monomer

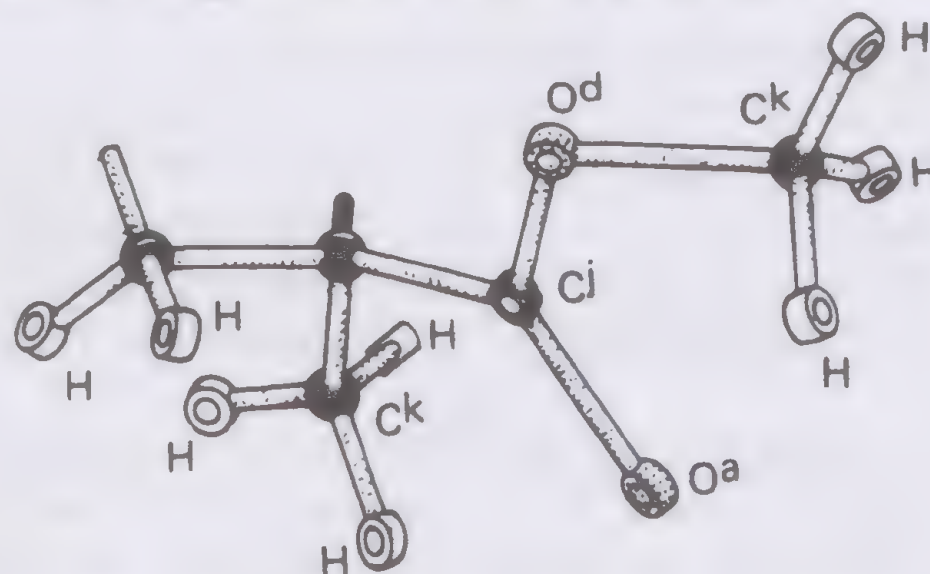


Figure 36 'Activated' perspex monomer

Figure 36 shows a way in which you can represent the 'Perspex' monomer after it has been activated by the catalyst.

Now, to make the model of the polymer 'Perspex' make two or three such monomer units and join them together to form a long chain, as shown in figure 37.

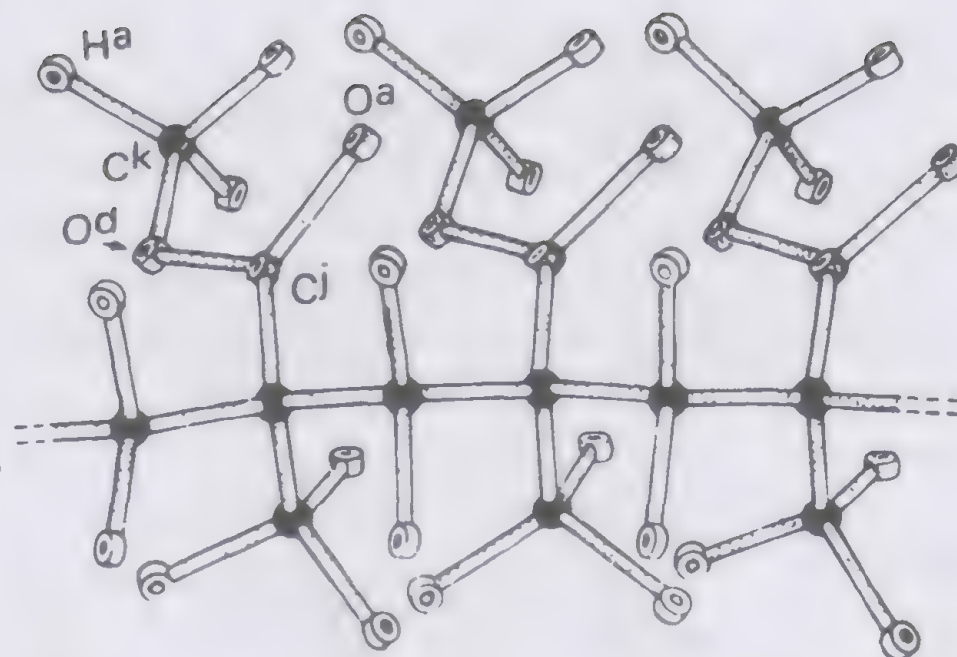


Figure 37 Perspex polymer

8 Optical isomerism

Introduction

When a molecule has a structure with no centre or plane of symmetry, it is said to be *asymmetric*. Substances whose molecules are asymmetric show *optical activity*, that is, they can rotate the plane of polarization of light, if a polarized beam is passed through a solution containing the substance.

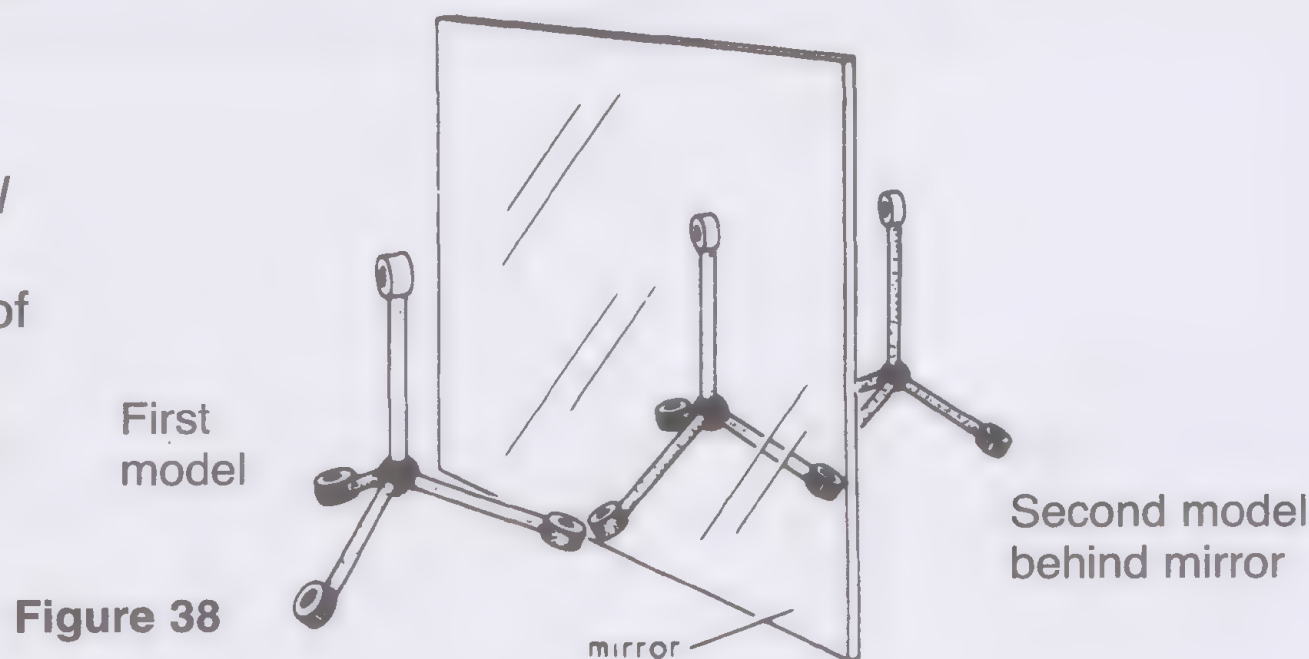
Asymmetric carbon atoms

Although the phenomenon of optical activity is not confined solely to carbon compounds it is very common here. To illustrate the effect take a tetrahedral carbon centre, C^k , and attach four straws. Now take any four differently coloured atoms and attach them to the straws in any relative position you like. The result illustrates an asymmetric molecule.

To demonstrate the asymmetry, make a second model *identical* with the first in every respect. Now take any two of the coloured atoms in the second model and exchange their positions. The second model is now the same as the first in all respects but one; it is the mirror image.

Take a piece of plane mirror large enough to enable you to view the entire reflection of one of the models, and place it vertically next to one of the models as in figure 38. Now adjust the second model so that it coincides exactly with the virtual image of the first model.

Two substances that are related in this mirror image fashion are said to be *optical isomers, or enantiomers*. Optical isomerism is a form of stereoisomerism, (page 14).



- 8.1 *Is it possible to rotate the position of the second model to make it appear identical with the first, without exchanging any groups?*
- 8.2 *Try to think of pairs of everyday objects that are related in the same way as stereoisomers.*
- 8.3 *Does chlorofluoromethane, CH_2FCl , show optical activity?*

To answer question 8.3, make a model of the molecule, set up the mirror as in figure 38, and then construct a second model to coincide with the mirror image of the first. Then find whether the pair of models are in fact identical by rotating them to see if their groups can be made to coincide.

For the molecule to be asymmetric and hence to show optical activity, there must be four different groups attached to the central carbon atom. In the case of CH_2FCl , two of the groups are identical (ie the two hydrogen atoms) and hence the substance is optically inactive.

Lactic acid (2-hydroxypropanoic acid)

To make instructions easier, the bonds are drawn in perspective in drawings of asymmetric molecules. Where a bond is shown thicker at one end than the other, the thicker end is taken to be closer to the observer. Using this convention, construct models of the two forms of lactic acid shown in figure 39.

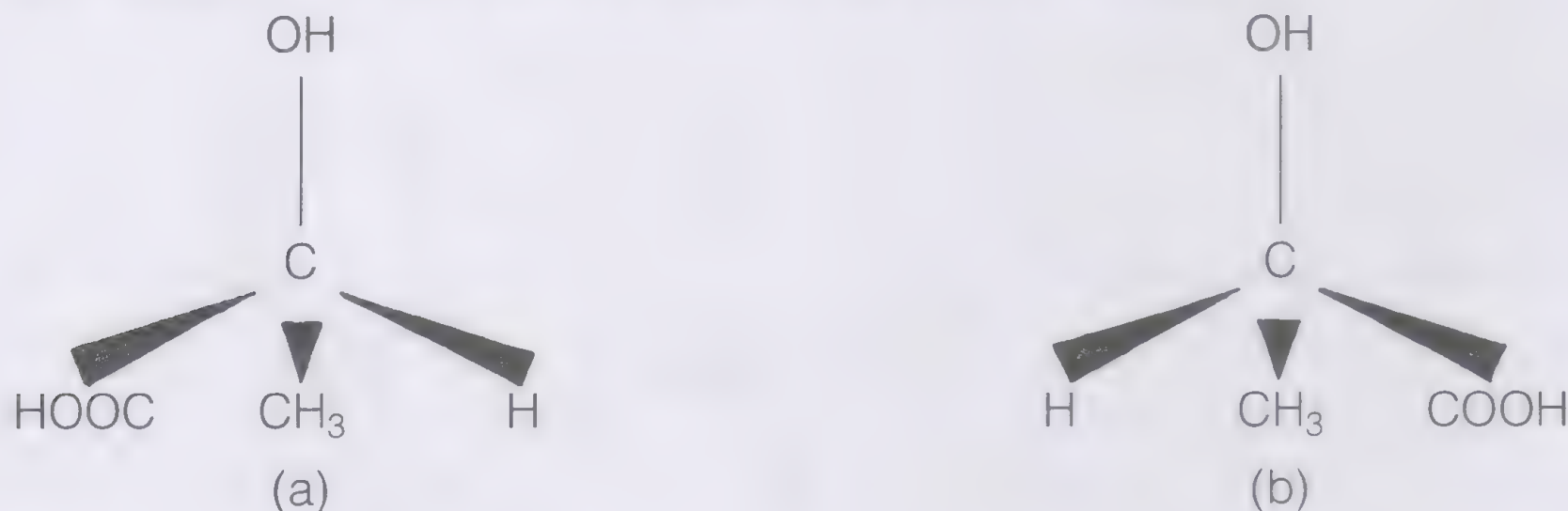


Figure 39 (a) D-lactic acid, (b) L-lactic acid

The carboxyl group, -COOH in figure 39, is constructed as shown in figure 40.

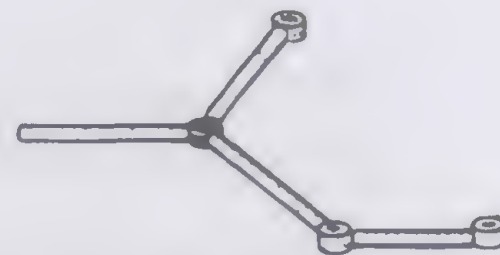


Figure 40 Carboxyl group

Figure 39(a) is called D-lactic acid.

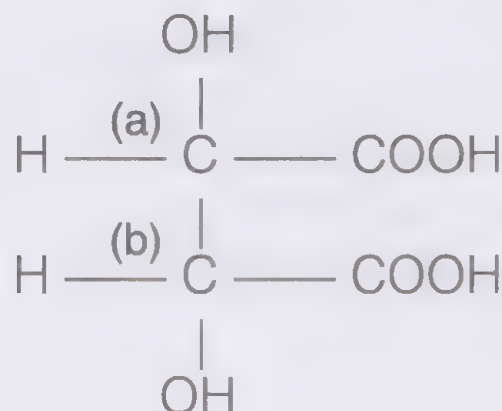
Figure 39(b) is L-lactic acid which has the opposite effect on the plane of polarized light. A 50:50 mixture of the two forms in solution has no effect on the plane of polarized light, and is called a *racemic mixture*.

8.4 *Is the carbon atom of the carboxyl group, COOH , asymmetric and capable of causing optical activity in a molecule? Make a model of hydroxyethanoic acid, $\text{CH}_2\text{OH.COOH}$, and check whether it is asymmetric.*

Optically active substances occur very commonly in living materials. For instance D-lactic acid is produced in muscle and is obtained from meat extract. L-lactic acid does not occur naturally. In general, L-isomers are uncommon in nature.

Molecules with two asymmetric carbon atoms

Tartaric acid (2,3-dihydroxybutanedioic acid) has the structure

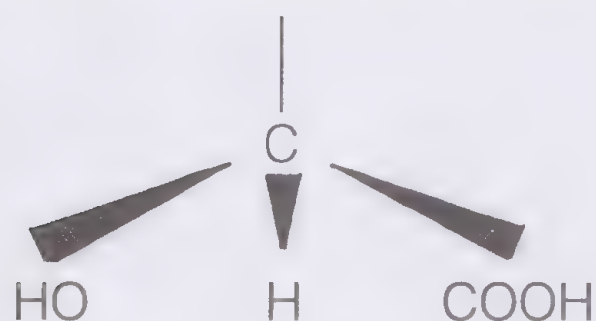


Note that both the carbon atoms (a) and (b) are asymmetric, ie they are each linked to four different atoms or groups. When a molecule has more than one asymmetric centre, further optical isomers are possible. To find out how many, proceed as follows.

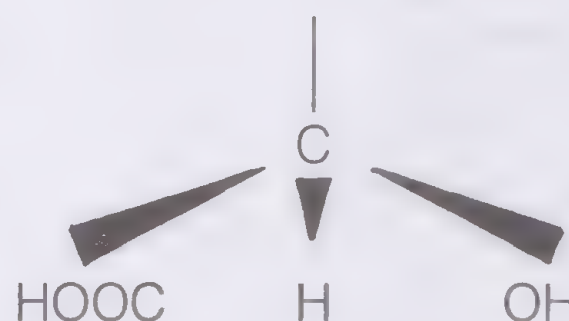
Make four models of one end of the tartaric acid molecule, as in figure 41 (a). Call these 'left-handed'. Now make four 'right-handed' forms as illustrated in figure 41 (b).

Now join up the halves as follows:

- (1) left-hand joined to right-hand form; make two models thus.
- (2) left-hand joined to left-hand form.
- (3) right-hand joined to right-hand form.



(a)



(b)

Figure 41

Take model (2) and place it next to a mirror, just as you did with the simple model described on page 31. Now take model (3) and place it behind the mirror. Adjust the relative positions of the groups so that the mirror image of (2) coincides exactly with (3). Note that in order to do this you may have to rotate the groups around the carbon-carbon bonds, and you may also have to rotate the carboxyl and hydroxyl groups themselves. (figure 42).

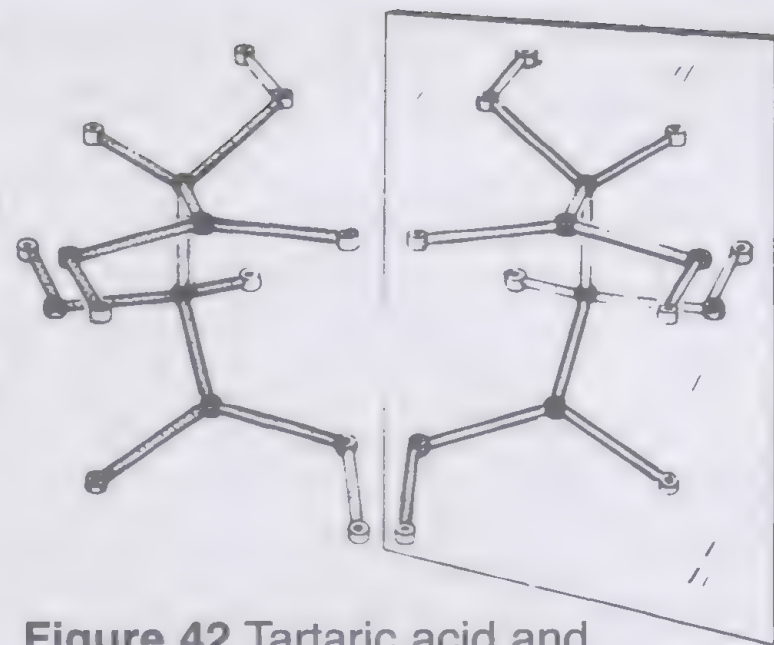


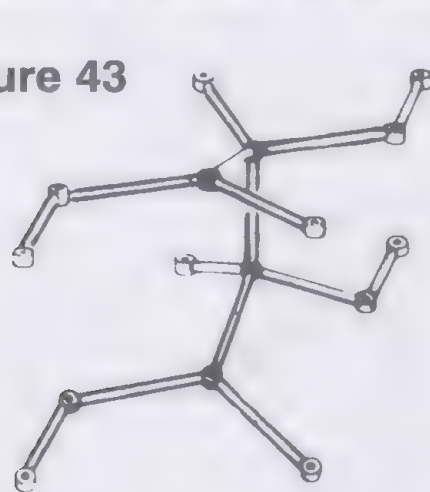
Figure 42 Tartaric acid and its mirror image

Configurations (2) and (3) are optically active forms of tartaric acid, ie solutions of each have equal and opposite effects on the plane of polarized light.

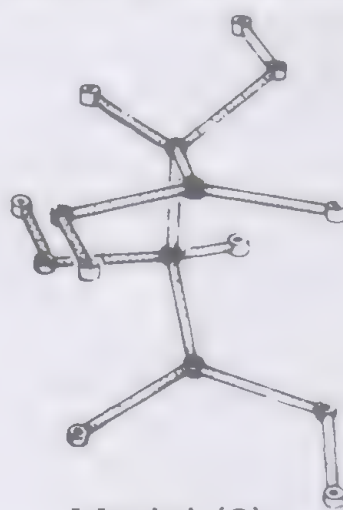
Now take your two models made as in (1). Place one by the mirror and attempt to arrange the other so that it coincides with the mirror image of the first. As before, it may be necessary to rotate the groups, but it is important not to disconnect any bonds.

Model (1) can be superimposed on its mirror image despite the fact that it has two asymmetric carbon atoms. The reason is that one end of the molecule is a mirror image of the other end, and the molecule as a whole has a plane of symmetry. (1) is known as the *meso* form: since the whole molecule is not asymmetric, it does not rotate the plane of polarized light. Figure 43 illustrates the three forms of tartaric acid.

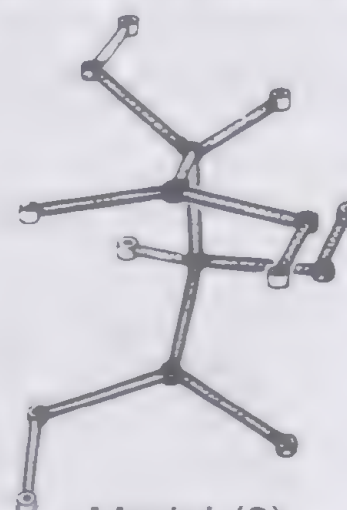
Figure 43



Model (1)
Meso tartaric acid



Model (2)
L-tartaric acid



Model (3)
D-tartaric acid

There is a fourth form of tartaric acid, the racemic acid produced by crystallizing tartaric acid from an equimolar mixture of the optically active forms (2) and (3). Its composition may be represented as one mole of each form plus two moles of water of crystallization.

The chemical properties of the D and L modifications of tartaric acid are identical. The physical properties (except for the action on polarized light) are also identical.

8.5 *There are two acids corresponding to the formula $\text{HOOC.CH}=\text{CH.COOH}$, depending, on whether the carboxyl groups are cis or trans to the double bond. Use models to predict which form of tartaric acid each will produce on oxidation with dilute potassium permanganate solution:*



Assume that the two hydroxyl groups are added from the same side of the double bond.

Summary

Stereoisomerism can be subdivided into geometrical isomerism and optical isomerism.

For a molecular substance to be optically active, it must possess molecules with no plane or centre of symmetry. Such molecules are non-superimposable on their mirror images.

A carbon atom becomes asymmetric if it is attached to four different groups.

Where two asymmetric centres exist in a molecule, it is possible for the molecule as a whole to possess a plane of symmetry and be optically inactive.

9 Simple inorganic molecules

Carbon dioxide, CO_2

The carbon atom in carbon dioxide contains two double bonds and no lone pairs.

Its shape is therefore linear, unlike H_2O which is bent (page 6). CO_2 has no lone pairs to distort its shape. To construct a model link a C^{k} centre to two O^{d} centres using flexible straws, (figure 45).

A simpler representation is to use rigid green straws linking a linear C^{b} centre to two O^{a} centres (cf simplified representation of carbonyl group, page 18).

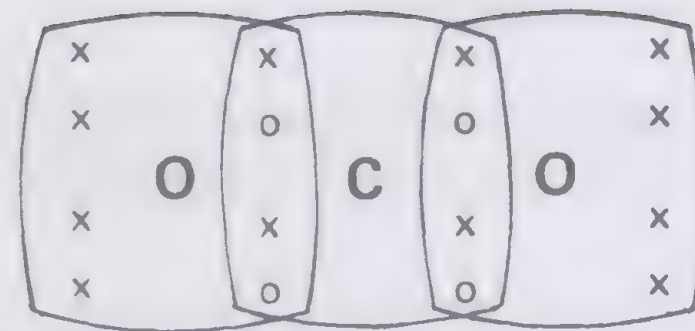


Figure 44 Carbon dioxide

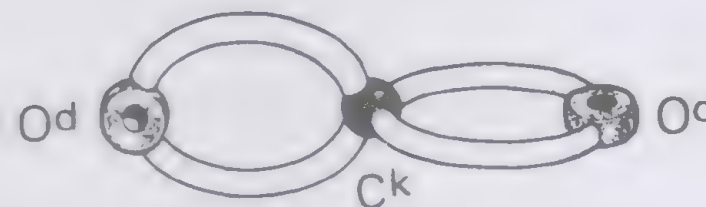


Figure 45 Carbon dioxide

9.1 Carbon disulphide is a volatile liquid of molecular formula CS_2 . Suggest a structure and electronic configuration for it, and make a model.

Carbonic acid, H_2CO_3

A solution of carbon dioxide in water contains carbonic acid, H_2CO_3 . The electronic configuration of the carbon atom is similar to that in ethene (page 12) with three bonds and no lone pairs. Make a model as in Fig 46. The carbonate ion, CO_3^{2-} , is completely symmetrical with 120° angles between all $\text{C}-\text{O}$ bonds.

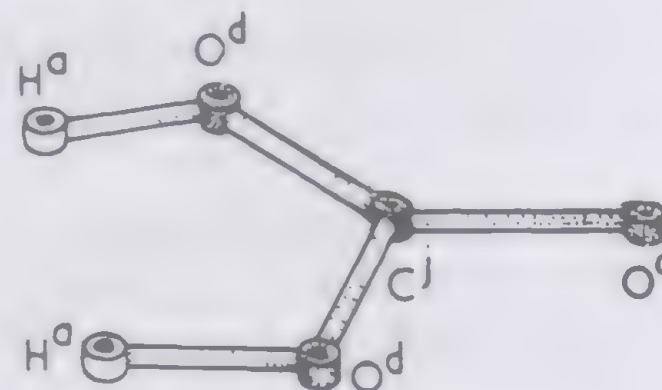


Figure 46 Carbonic acid

Molecules containing 'tetrahedral' nitrogen

The directions of the bonds around a nitrogen atom depend on their number, and upon the number of lone pairs.

Models of ammonia, NH_3 , and the ammonium ion NH_4^+ , were described on page 5. The principles underlying shapes of molecules were also dealt with on page 5. For further practice, construct a model of methylamine CH_3NH_2 (figure 47).

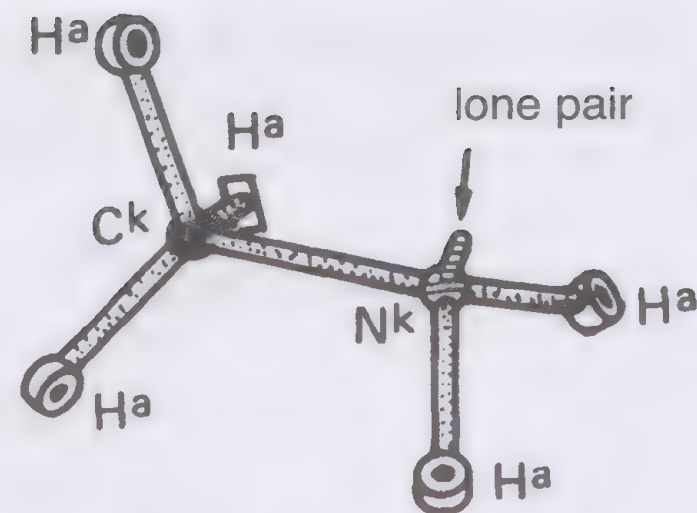
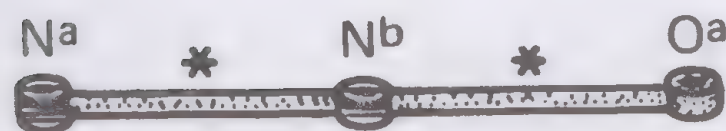


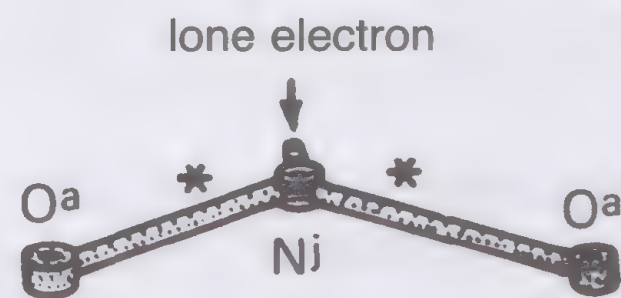
Figure 47 Methylamine

Some oxides of nitrogen

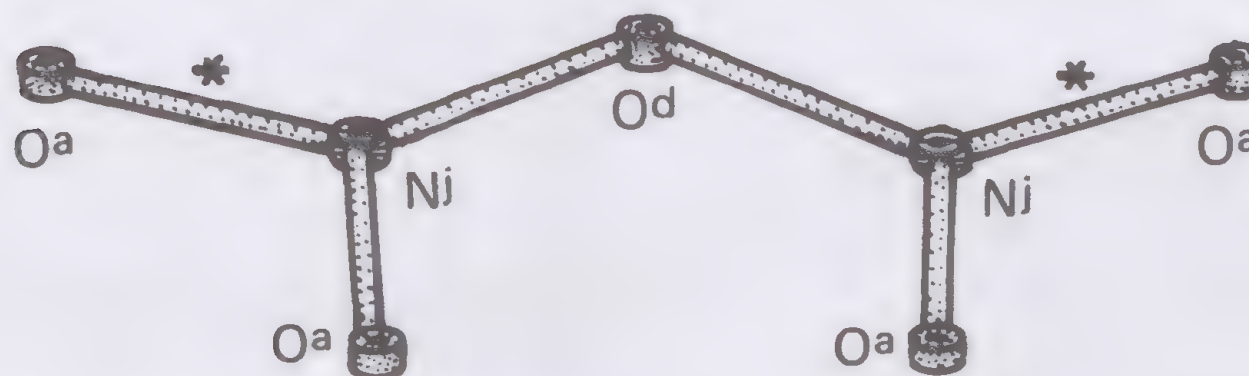
Figure 48 shows the structures of some common oxides of nitrogen, labelled with the code letters of the atomic centres to be used in the construction of the models. It is simpler to omit any attempt at representing double bonds. The bonds marked * may be considered as double bonds. Also, it is simpler to assume that all the bonds are the same length, although in fact this is not the case.



(a)



(b)



(c)

Figure 48 (a) Dinitrogen monoxide, (b) nitrite [nitrate (III)] ion, (c) dinitrogen pentoxide

Nitric acid [nitric (V) acid] HNO_3

Figure 49 shows the structure of nitric acid, together with code letters of atoms to be used in constructing a model. Also shown is nitrate ion, NO_3^- .



Figure 49 (a) Nitric acid, (b) nitrate ion

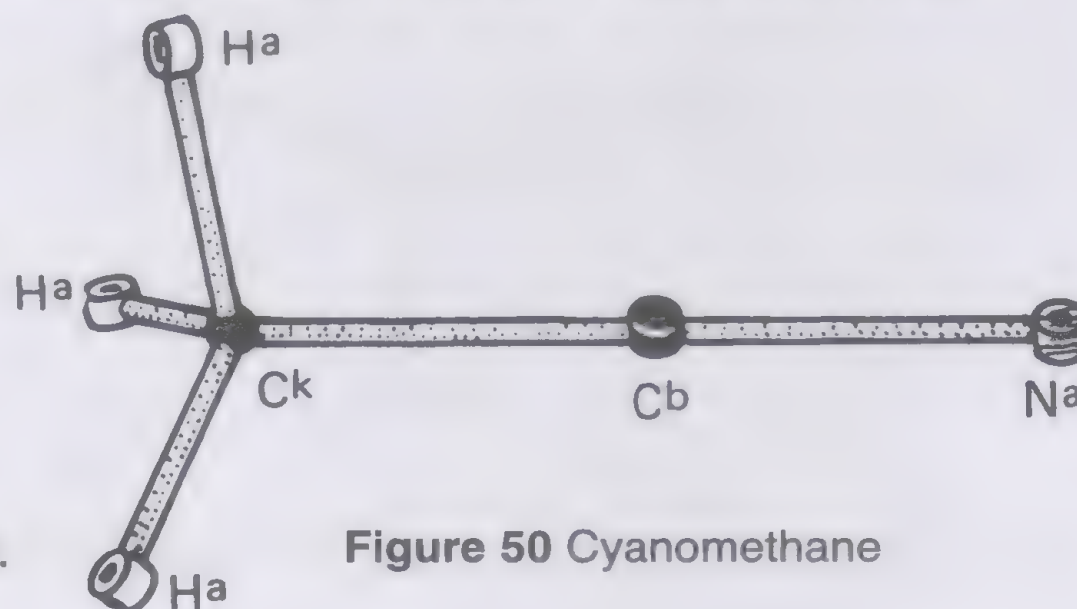
Nitrous acid [nitric (III) acid], HNO_2

Nitrous acid contains a lone pair. Its structure may be derived from that of nitric acid simply by removing an oxygen atom together with its bond, and leaving a free prong to denote the lone pair. The nitrite ion [nitrate (III) ion], NO_2^- , may be derived similarly from the nitrate ion, NO_3^- .

Hydrogen cyanide, HCN

Hydrogen cyanide has the structure $\text{H} - \text{C} \equiv \text{N}$. Note that the carbon atom is linear just as in ethyne, $\text{H} - \text{C} \equiv \text{C} - \text{H}$ (page 14). Construct a model of hydrogen cyanide, using H^a , C^b and N^a atoms. The cyanide ion, CN^- , may be represented simply by detaching the hydrogen atom together with its bond. (See also cyano-complexes, page 43 fig.61).

Organic cyano-compounds, also known as nitriles, may be regarded as derived from hydrogen cyanide by the replacement of the hydrogen atom by an alkyl or other group. For instance, figure 50 illustrates cyanomethane, CH_3CN . Strictly, the $\text{C} - \text{N}$ bond is a triple bond $\text{C} \equiv \text{N}$.



White phosphorus, P_4

Figure 51 shows a model of the P_4 molecule. Note that bond distortion occurs and flexible straws have to be used. Use four P^k centres linked by flexible straws.

Phosphoric acid, H_3PO_4

Phosphoric acid has a structure in which the central phosphorus atom is tetrahedral.

Figure 52 shows its structure, together with the bonds and atomic centres required to construct a model. Note that, for the sake of simplicity, no attempt is made to distinguish between double and single bonds.

The ions, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} may be constructed by removing in turn hydroxyl groups $-OH$ and replacing each with an oxygen centre, O^a .

Phosphorus (V) oxide. P_4O_{10}

This may be constructed as in figure 53, using four tetrahedral phosphorus centres, P^k , six diunivalent oxygen centres, O^d , and four oxygen centres, O^a . The whole structure is based upon the tetrahedron. Phosphorus (V) oxide is the acid anhydride of phosphoric acid. Note that this structure is not unlike that of diamond, in which tetrahedral bonds also determine the shape.

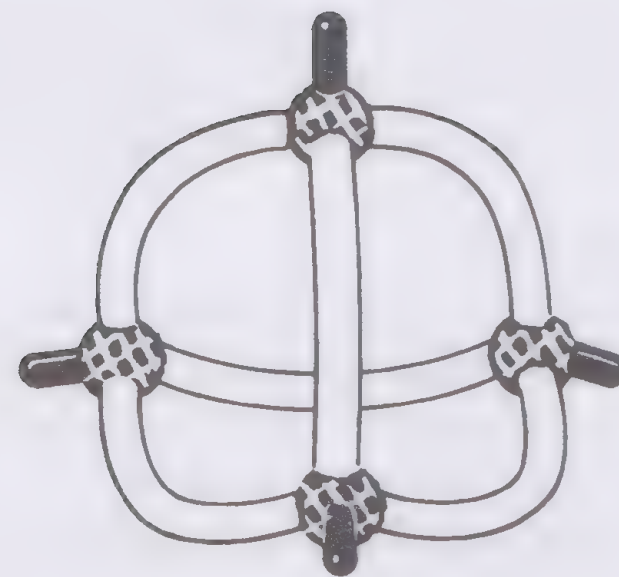


Figure 51 The P_4 molecule

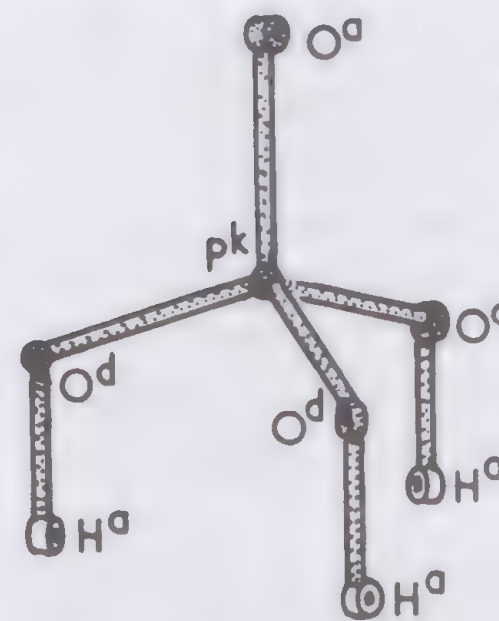


Figure 52 Phosphoric acid

9.2 Heptaoxodiphosphoric acid has the molecular formula $H_4P_2O_7$. It may be formed by the action of water on phosphorus (V) oxide. Suggest a structure for it, and make a model.

Phosphorus (III) oxide, P_4O_6

A model of phosphorus (III) oxide can be constructed by removing the four oxygen centres, O^a , from the corners of the phosphorus (V) oxide model constructed as in figure 53.

Sulphur

When a sulphur atom forms two single bonds, two lone pairs are also present. Consequently, the bonds are at an angle of about 100° to one another. The commonest molecular form of sulphur is the ring form, S_8 , in which eight atoms with bonds about 100° apart (S^c) unite to form a puckered ring structure, figure 54. Construct a model of this.

The above ring form is present in orthorhombic and monoclinic sulphur crystals, and persists just above the melting point. Further heating causes the rings to open and link to form polymeric chains. Open an S_8 ring model, and note the zig-zag nature of the chain formed. Chain molecules of this type constitute plastic sulphur.

Hydrogen sulphide, H_2S

The shape of the hydrogen sulphide molecule is similar to that of the water molecule, but the bond angle is slightly different.

9.3 Explain why the H_2S molecule is bent rather than linear.

9.4 Hydrogen forms polysulphides, H_2S_x , where $x = 1$ to about 6. Suggest structures for these, and construct models.

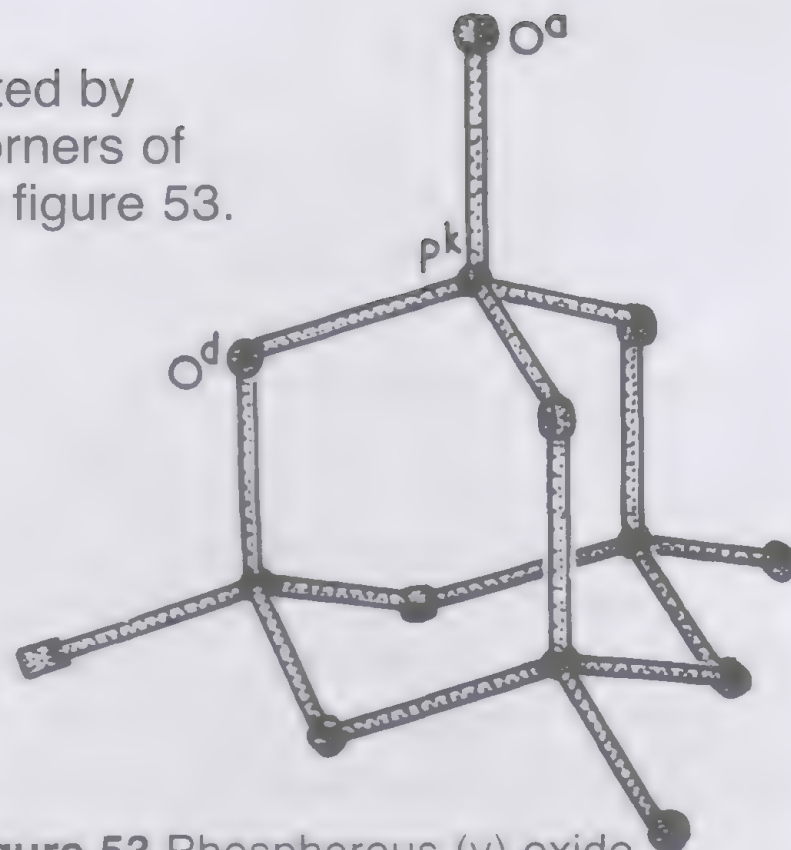


Figure 53 Phosphorous (v) oxide

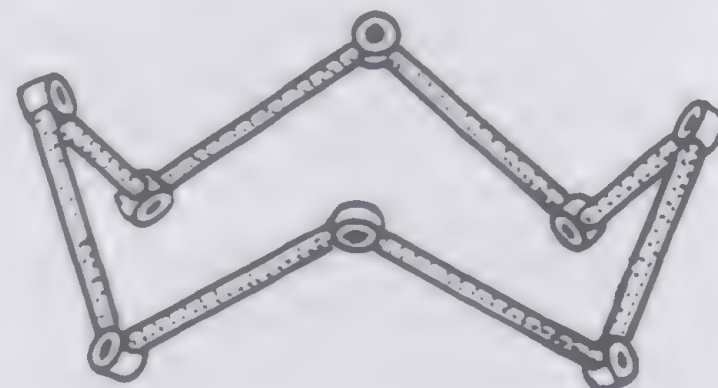


Figure 54 Sulphur ring

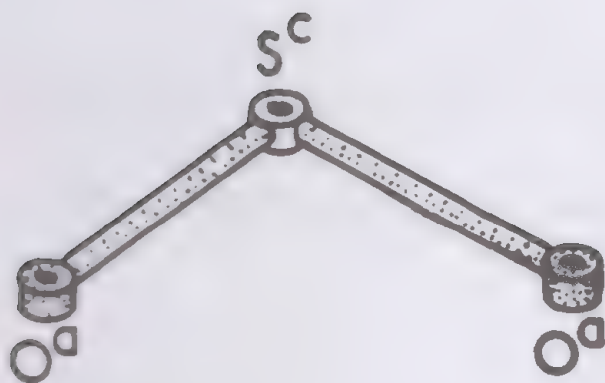


Figure 55 Sulphur dioxide

Sulphur dioxide, SO_2

Sulphur dioxide has a lone pair of electrons on the sulphur atom and is therefore bent. To construct a model, proceed as in figure 55.

Sulphuric acid, H_2SO_4

Sulphuric acid contains a tetrahedral atom at the centre (cf phosphoric acid, page 39). To construct a model of it, proceed as in figure 56.

The sulphate ion, SO_4^{2-} may be derived from this structure by removing two hydrogen ions,

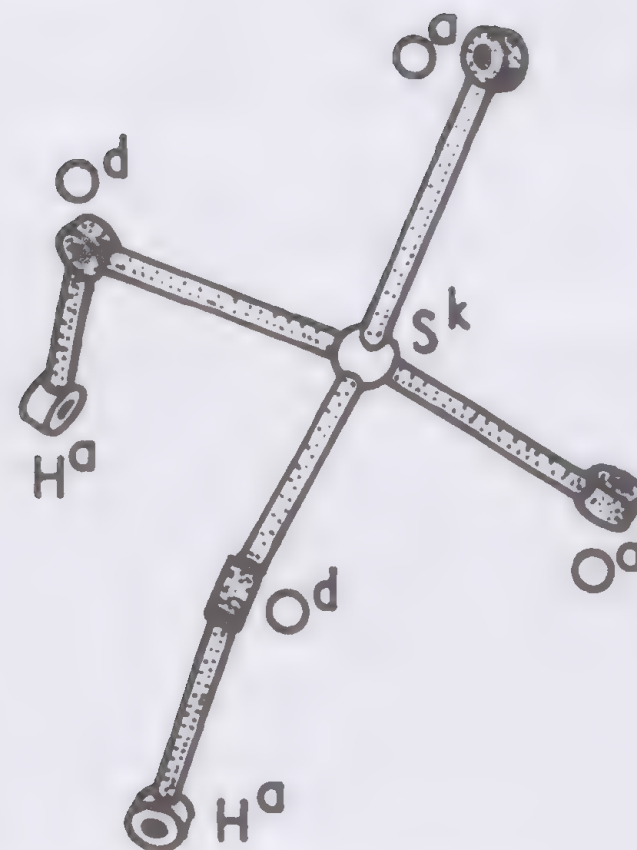


Figure 56 Sulphuric acid

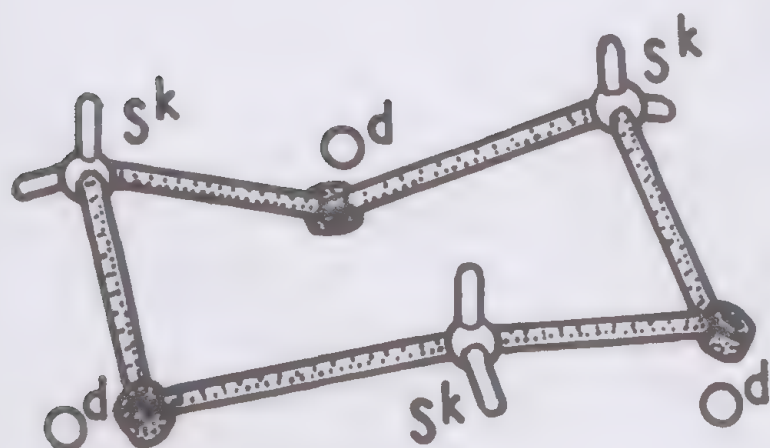


Figure 57

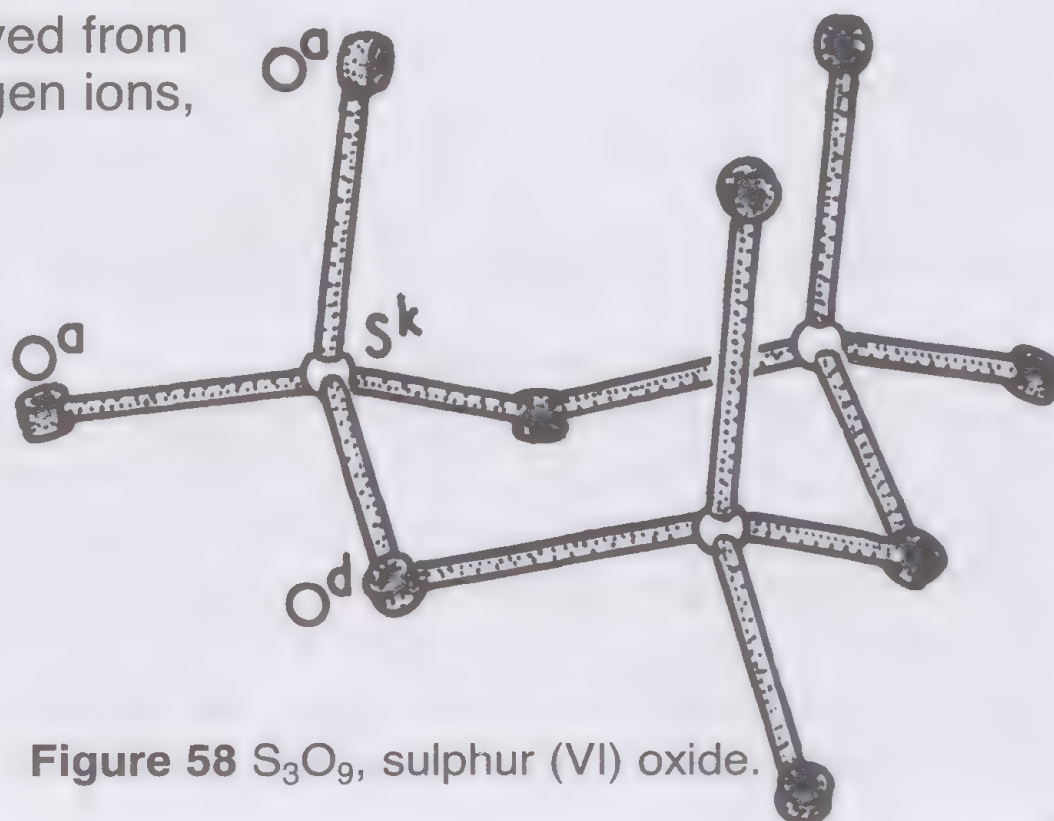


Figure 58 S_3O_9 , sulphur (VI) oxide.

H⁺: to achieve this, detach the two hydroxyl-groups –OH and replace each with an oxygen centre, O^a. Note that the resultant structure has complete tetrahedral symmetry.

9.5 Name another ion which has the same structure, and also the same electronic configuration, as the sulphate ion SO₄²⁻

Sulphur trioxide [sulphur (VI) oxide], SO₃

Strictly speaking the name 'sulphur trioxide' should only be applied to the molecular species SO₃, which only exists at elevated temperatures in the vapour phase. Its shape is based upon a planar triangle with the sulphur atom at the centre. At room temperature 'polymeric' forms exist in the solid state, such as S₃O₉. To construct a model of the latter you will need three sulphur centres S^k, three oxygen centres O^d, and six oxygen centres O^a. Start by constructing a ring using the three S^k and three O^d centres as in figure 57. Then add the six O^a centres as in figure 58. Note that the resultant structure is in some ways analogous to that of P₄O₁₀.

10 Complex ions

Principles underlying shape

The shape of a complex ion depends upon the number of ligands, and also on factors such as the number of non-bonding electrons present in the uppermost energy levels of the metal atom. Most hexadentate complexes (ie with six points of attachment) are approximately octahedral, and may be represented by using the silver octahedral atom centres, M^l. Tetradentate complexes (four points of attachment) are sometimes tetrahedral and some-times square planar. The latter may be represented in model form by using the octahedral atom models, but omitting to put groups along one axis.

Simple octahedral complexes

Figures 59, 60 and 61 represent respectively the complex ions Cr(H₂O)₆³⁺, Co(NH₃)₆³⁺, and Fe(CN)₆³⁻, to illustrate the general principles. Note that the same silver octahedral atomic centre must be used in every case. In each case, start by constructing models of the ligands, for instance six water molecules using tetrahedral oxygen centres, O^k, or six ammonia molecules using tetrahedral nitrogen centres N^k. Attachment to the central metal atom is then made using straws attached to one of the prongs representing a lone pair on each ligand.

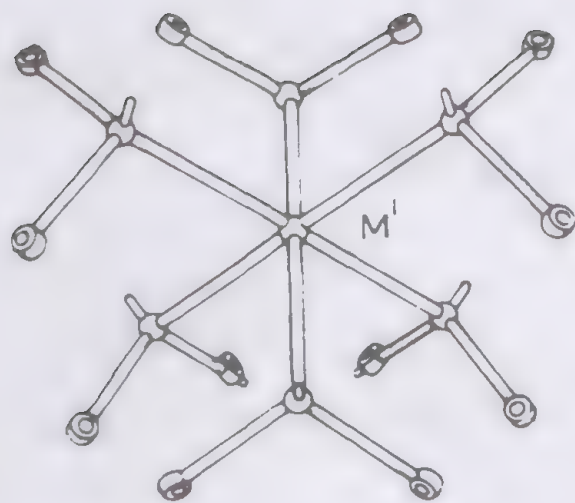


Figure 59
Hexa-aquachromium(III)
ion

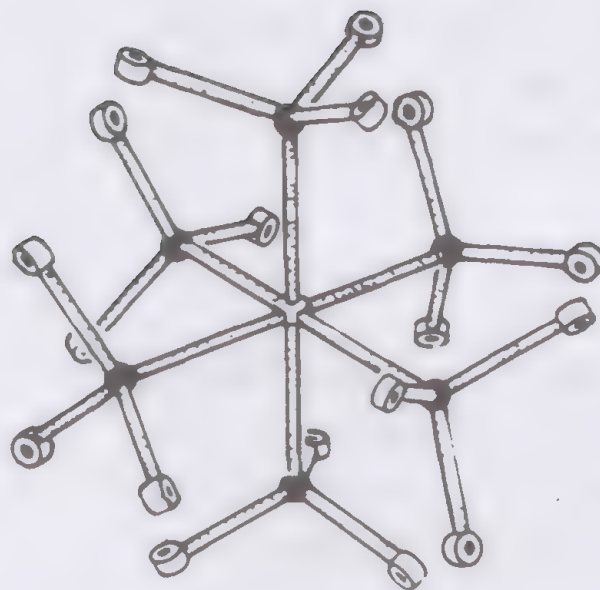


Figure 60
Hexa-amminecobalt (III)
ion

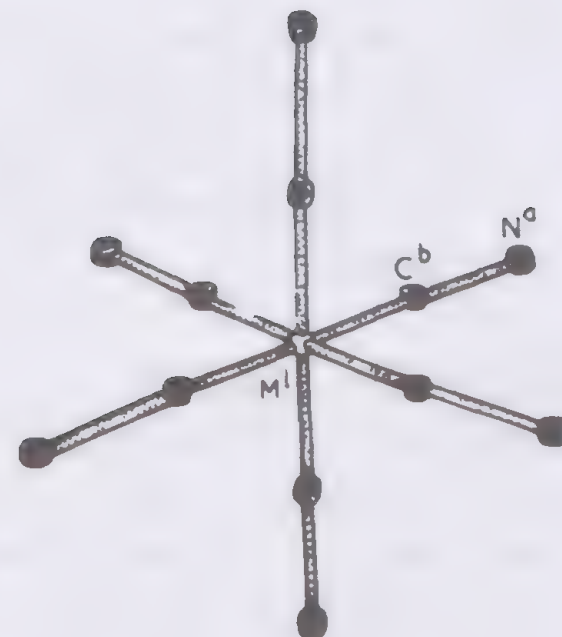


Figure 61
Hexacyanoferrate (III)
ion, multiple bonds
have been omitted

Simple tetrahedral complexes

A simple example is tetramminozinc(II). Proceed as in figure 60 above, but use instead a silver tetrahedral centre, M^k and attach only four ammonia molecules. Another interesting example is the uncharged complex, tetracarbonylnickel(0), $Ni(CO)_4$. The ligand here is carbon monoxide, attached to the nickel atom via the lone pair on the carbon atom. Construct four carbonyl ligands using linear carbon atoms C^b linked to oxygen centres O^a . Attach the ligands to a silver tetrahedral centre M^k (figure 62).

Simple square planar complexes

The ion $Cu(H_2O)_4^{2+}$ is square planar. Remove two ligands from one axis of your model of $Cr(H_2O)_6^{3+}$. The two spare prongs represent the location of one spare non-bonding electron (figure 63).

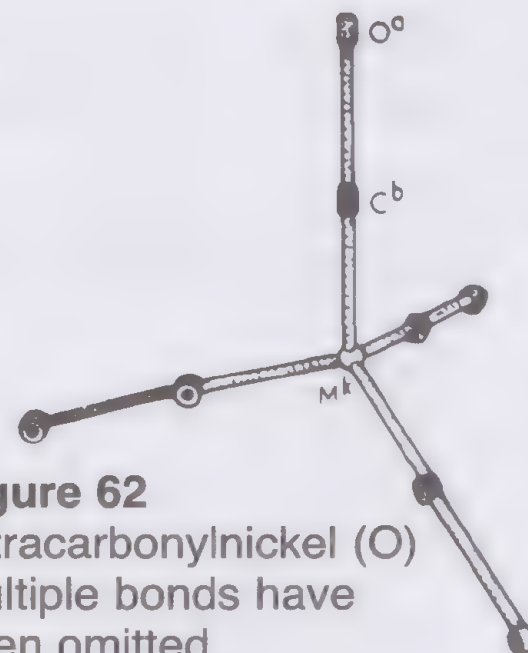


Figure 62
Tetracarbonylnickel (0)
Multiple bonds have
been omitted

10.1 The complex ion $\text{Pt}(\text{H}_2\text{O})_2\text{Cl}_2^{2+}$ can exist in two isomeric forms. What does this suggest concerning the shape of the ion? What is the relationship between the isomeric forms?

Bidentate ligands

A ligand which can form two points of attachment with the central atom is said to be bidentate. An example is 1,2-diaminoethane (ethylenediamine), $\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$. Construct three models of this. For each you will need two C^k , two N^k and eight H^a .

Take a silver octahedral centre, M^I , and attach the three ligands to it. The resultant model could represent for instance $\text{Co}(\text{en})_3^{3+}$, where en = 1,2-diaminoethane. (figure 64).

10.2 Is it possible to construct isomers of $\text{Co}(\text{en})_3^{3+}$, assuming the configurations of individual atomic centres to be unchanged?

Now construct models of $\text{Zn}(\text{en})_2^{2+}$ (tetrahedral) and $\text{Cu}(\text{en})_2^{2+}$ (square planar).

10.3 Are either of the above complex ions capable of existing as isomers?

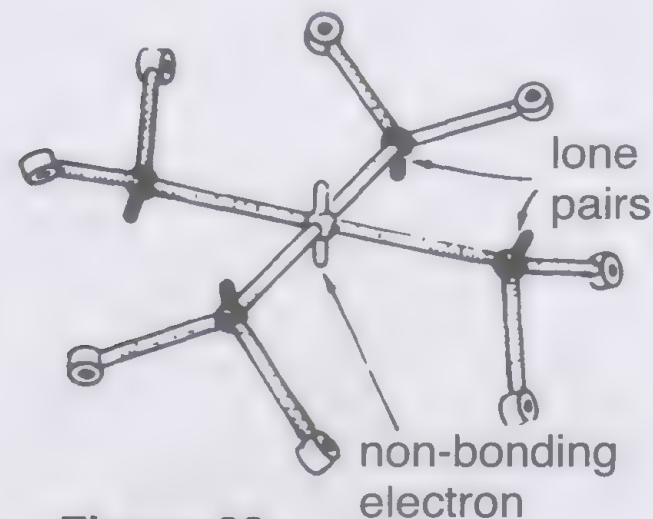


Figure 63
Tetra-aquacopper (II) ion

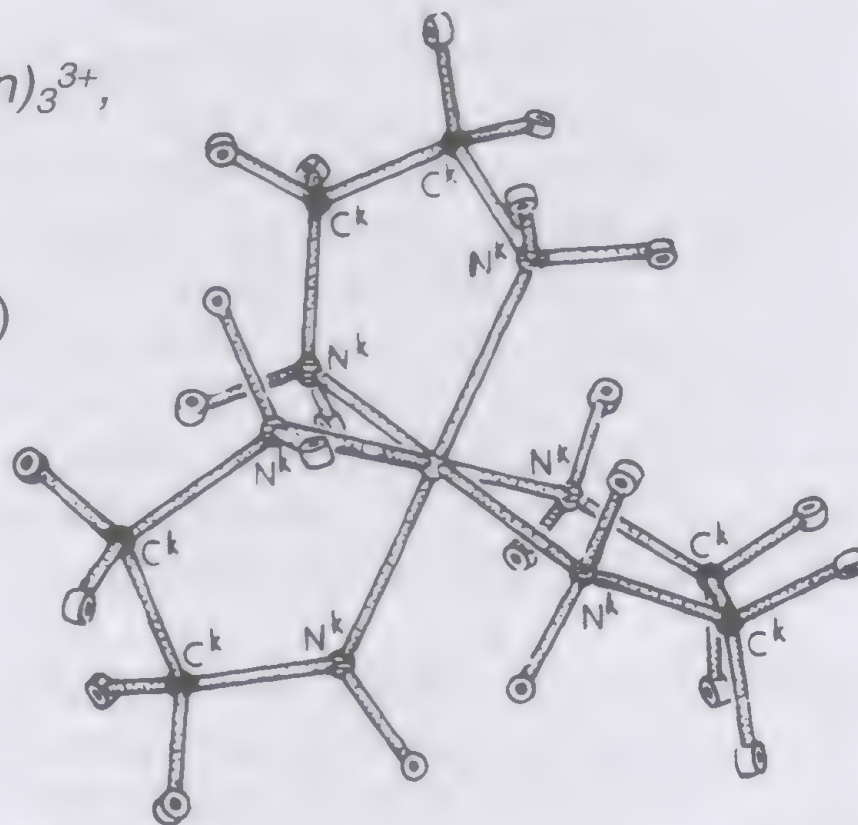


Figure 64
Tris(ethylenediamine) cobalt (III) ion

Notes and answers to questions

1 Principles of molecular shape

1.1 The calculated angle is $109^{\circ} 28'$

1.2 No

1.3 Pyramidal.

1.4 Tetrahedral: NH_4^+ is isoelectronic with CH_4 and therefore has the same shape

1.5 (a) Bent, for the same reason that H_2O is bent. (b) Pyramidal, since it is isoelectronic with NH_3 (see Question 1.3)

1.6 PCl_3 has a pyramidal structure like ammonia and its electronic structure is as shown in diagram 1.

1.7 The respective electronic structures are as diagrams 2 and 3.

Since both of these molecules have five repelling electron pairs, their shapes will be based on the trigonal bipyramid. ClF_3 is in fact T-shaped with two 'equatorial' lone pairs:



SF_4 has a distorted shape with one equatorial lone pair:

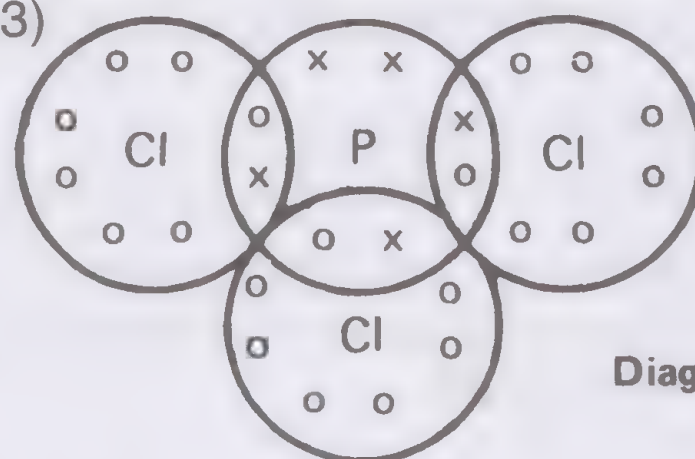
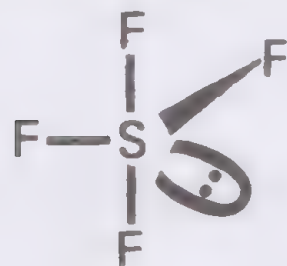


Diagram 1

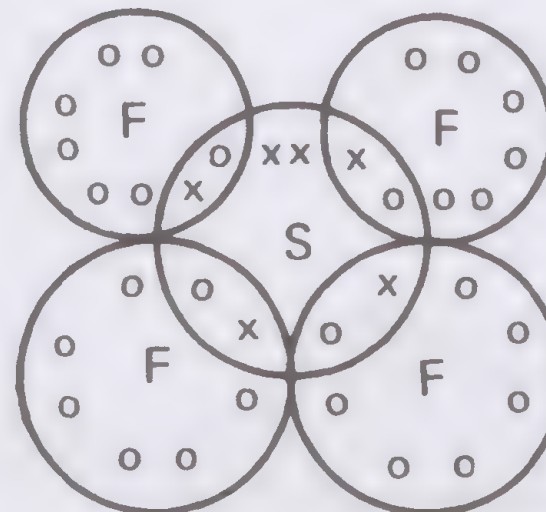


Diagram 2

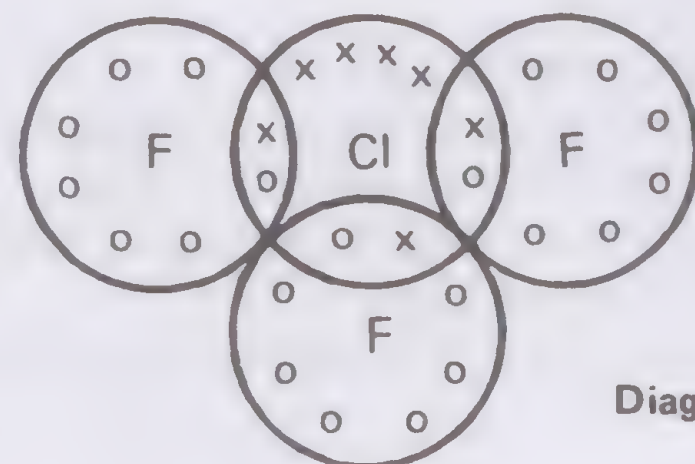
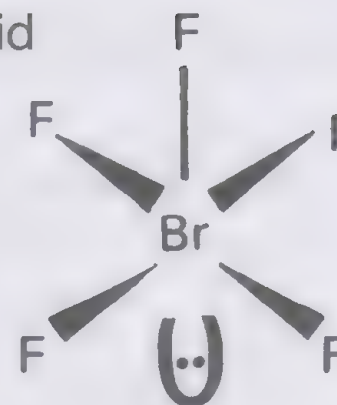


Diagram 3

1.8 The theoretical angle is 90°

1.9 BrF_3 is thought to have the shape of a square pyramid



2 Saturated hydrocarbons

2.1 The theoretical angle is $109^\circ 28'$

2.2 Structures (b) and (c) are the same

2.3 Two

2.4 Only one

2.5 Two

2.6 Four (1,1; 2,2; 1,2 and 1,3)

2.7 All these structures are in fact the same

2.8 No

2.9 18, one of which is octane.

(The number of isomers of $\text{C}_{40}\text{H}_{82}$ is 62,491,178,805,831!)

3 Unsaturated hydrocarbons

3.1 The atom centres lie in a plane, though the bent straws project above and below the plane

3.2 Hardly at all

3.3 Four

3.4 Eight, as in ethane

3.5 No

3.6 Only one

3.7 No

4 Cyclic hydrocarbons

4.1 $109^\circ 28' - 108^\circ = 1^\circ 28'$

4.2 No, because the ring is flat and rigid

4.3 Two (*cis* and *trans* isomers)

4.4 Puckered

4.5 Tetrahedral, ie $109^\circ 28'$

4.6 Slightly, ie from one ring conformation to another

4.7 $109^\circ 28'$, the tetrahedral angle

4.8 It is difficult to join the ends of a long chain to form a ring, since they are initially so far apart

4.9 The bond angle is strained to 90° from the tetrahedral angle

5 Functional groups in organic chemistry

- 5.1 Because the oxygen atom has two lone pairs
- 5.2 Two
- 5.3 Two: $\text{CH}_3.\text{O}.\text{CH}_2.\text{CH}_2.\text{CH}_3$ and $\text{CH}_3.\text{O}.\text{CH}(\text{CH}_3)_2$
- 5.4 Three: two alcohols and one ether
- 5.5 14: eight alcohols and six ethers (excluding optical isomers)

6 Benzene and its derivatives

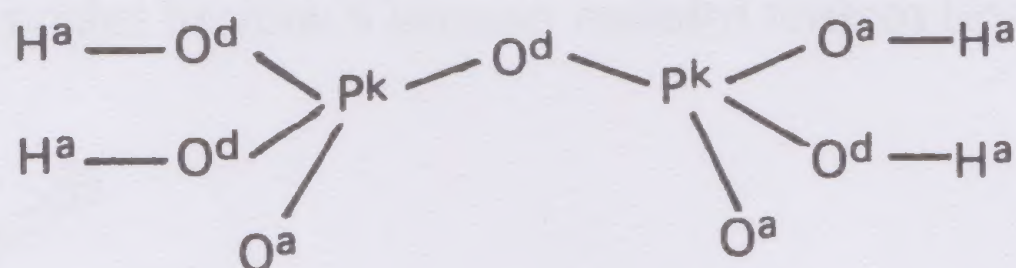
- 6.1 No
- 6.2 Three: 1,2; 1,3 and 1,4
- 6.3 Three, named as for question 6.2
- 6.4 Tetrahedral. No
- 6.5 Three. (1,2-dimethylbenzene, 1,3-dimethylbenzene and 1,4-dimethylbenzene)

8 Optical isomerism

- 8.1 No
- 8.2 Pair of gloves, shoes, etc
- 8.3 No
- 8.4 No, glycolic acid is not asymmetric
- 8.5 The *cis* acid oxidizes to *meso*-tartaric. The *trans* acid oxidizes to an equimolar mixture of D- and L-tartaric acid (racemic mixture)

9 Simple inorganic molecules

- 9.1 Linear structure, and similar electronic configuration to CO_2
- 9.2 Use two P^k centres, five O^d and two O^a and four H^a linked as follows:



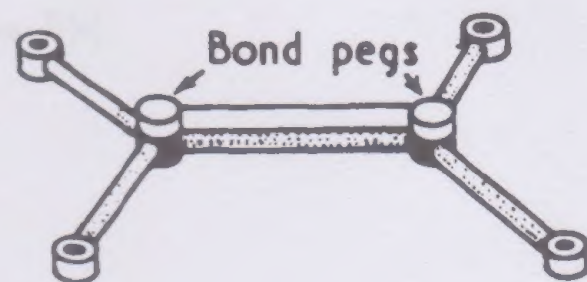
- 9.3 Because H_2S has two lone pairs on the sulphur atom
- 9.4 Use a short chain of S^c centres, linked by straws, with an H^a centre at each end of the chain
- 9.5 PO_4^{3-} and ClO_4^-

10 Complex ions

- 10.1 It cannot be tetrahedral (it is in fact planar)
- 10.2 No
- 10.3 No

Manufacturer's note

"Orbit" sets also include pegs for building multiple bonds in a different form from that shown in the text. The advantage of these pegs is that they show the presence of the multiple bond and restrict rotation around it without taking up a lot of space.



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polysaccharides
ribonucleic acid, RNA
deoxyribonucleic acid, DNA

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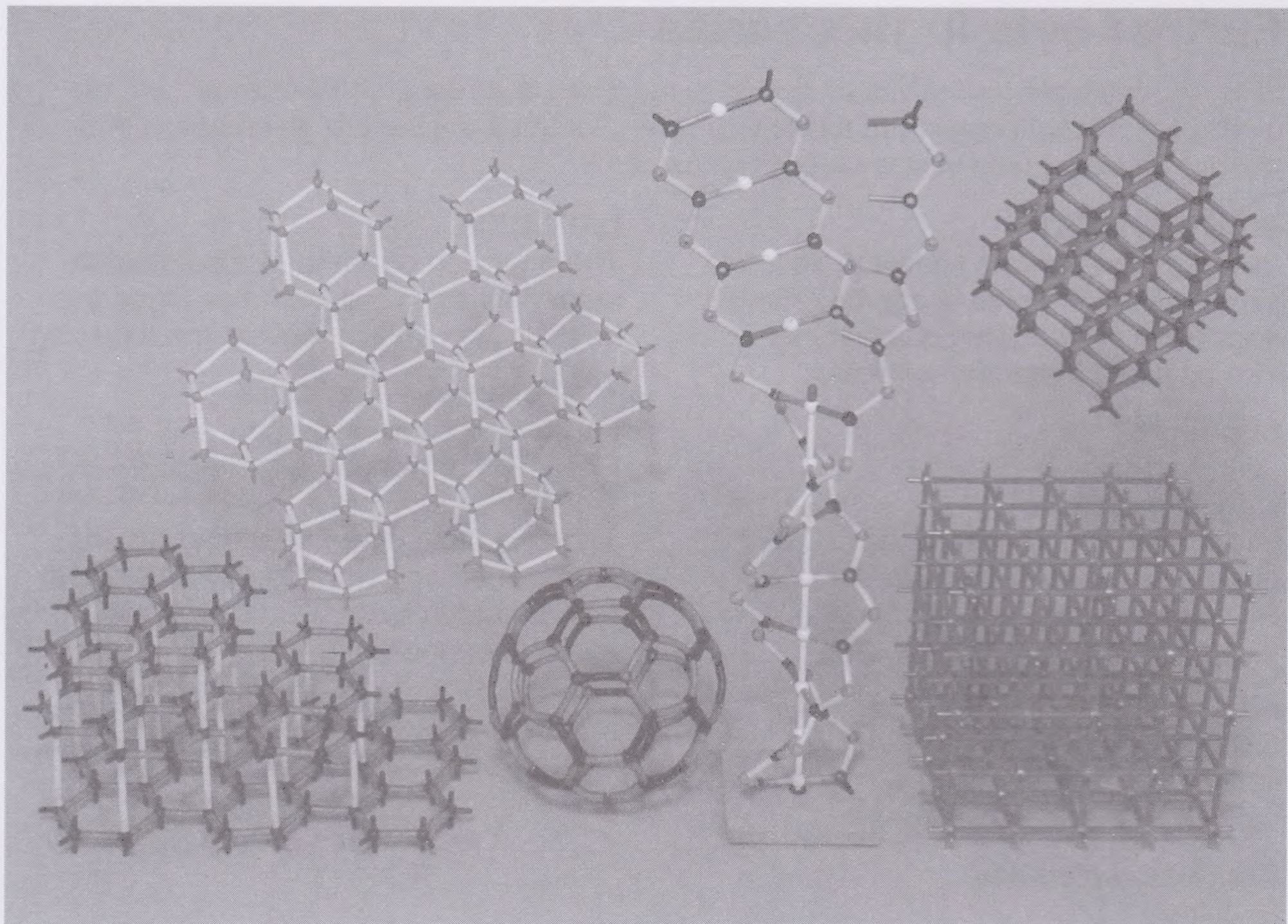
The seven crystal systems
Forms of carbon-diamond
Forms of carbon-graphite
Metals
Sodium chloride and 6:6 cubic lattices
Zinc blende and wurtzite, 4:4 structures
8-coordinated ionic structures Rutile
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SPARE PARTS

Additional atom centres, bonds of various lengths, bonding pegs, p-orbital shapes, books and other accessories are available from your supplier or Cochranes of Oxford Ltd.



Models of graphite, ice, carbon 60, DNA-RNA, sodium chloride and diamond built in the Orbit System, in this series there are also models of iron, copper and magnesium. They can each be bought as a kit of parts with assembly instructions or ready assembled. There is also available a series of model kits where the size of the model in numbers of unit cells is considerably larger. This series includes kits to make diamond, graphite, Fullerene 60 and 70, sodium chloride, ice, zinc blende, wurtzite, rutile, lead iodide, zeolite, quartz, calcite, mica, fluorite, caesium chloride, iron, magnesium and copper. For full details of these and our range of molecular building systems see our website www.cochranes.co.uk.